

2.5–3.1, 3.53 (d, $J = 4$ Hz), and AB system with doublets centered at 3.75 and 4.17 ($J = 12$ Hz), 5.97 (d, $J = 4$ Hz), 7.0–7.3 (m). This crude product was dissolved in 150 ml of absolute EtOH at room temperature, and 700 ml of water was added to give yellow solid, mp 102–130°, the nmr spectrum of which was almost indistinguishable from that of pure **3**. Recrystallization from hot 95% EtOH gave pure **3**, mp and mmp 149–151°.

Independent Synthesis of Diaminobenzil 3.—A solution of 32.76 g (0.205 mol) of bromine in 100 ml of CCl₄ was added dropwise during 4 hr to a hot, stirred solution of 23.8 g (0.1 mol) of 2,2'-dimethylbenzil^{5b} in 500 ml of CCl₄ containing a few crystals of benzoyl peroxide; during this time, the reaction mixture was irradiated with a 2 50-W sun lamp. The product crystallized on cooling (ice bath) and was filtered. It was then washed with cold CCl₄ to give 17.32 g (44%) of the crude 2,2'-di(bromomethyl)benzil (**4**): mp 145–155° (decomposes to a black tar); ir (CHCl₃) 5.97 μ (C=O); nmr (CDCl₃) δ 5.04 (s, 4 H, 2Ar-CH₂Br), 7.2–7.7 (m, 8 H). The nmr spectrum of the filtrate obtained on removing crude **4** showed peaks indicating the presence of non-, mono-, and dibrominated methyl groups in the mixture of benzils remaining. Three crystallizations of **4** from CCl₄ gave a sample: mp 155–156° (decomposes to a black tar); mass spectrum, m/e (relative intensity) 398 (0.08), 396 (0.14), 394 (0.08), 318 (0.2), 317 (1.2), 316 (1.7), 315 (1.2), 314 (1.4), 200 (10), 199 (100), 198 (10), 197 (100), 119 (15), 118 (93), 90 (37), 89 (19). The sample was not analytically pure.

The crude dibromobenzil **4** (1.25 g, 3.2 mmol) was added to anhydrous dimethylamine (ca. 40 ml) and the mixture stirred at reflux (Dry Ice-acetone condenser) for 2 hr. The mixture was poured into water, dilute NaHCO₃ solution was added, and the aqueous mixture was extracted with ether. The ethereal extracts were dried and evaporated. The residue was recrystallized from 95% EtOH to give 0.72 g (70%) of **3** as yellow needles, mp and mmp 149–151°. The infrared spectra of the two samples were indistinguishable.

Failure of Autoxidation of Benzoin in the Presence of a Tertiary Amine.—A solution of benzoin (2.12 g, 0.01 mol), KCN (0.5 g), and benzyldimethylamine (1.35 g, 0.01 mol) in 95% EtOH (40 ml) was refluxed for 24 hr, cooled, and the precipitate (white needles) was filtered to give 1.30 g (62%) of benzoin, mp and mmp 132–133°. Vpc of the mother liquor showed no peak for benzil, but did show a peak for benzoin. Probably more benzoin could have been recovered from the mother liquor.

Registry No.—**1**, 19886-78-3; **3**, 19922-49-7; **4**, 19886-79-4; **6**, 19886-80-7; benzoin, 119-53-9.

Bromination of Silver and Sodium Stilbenecarboxylates

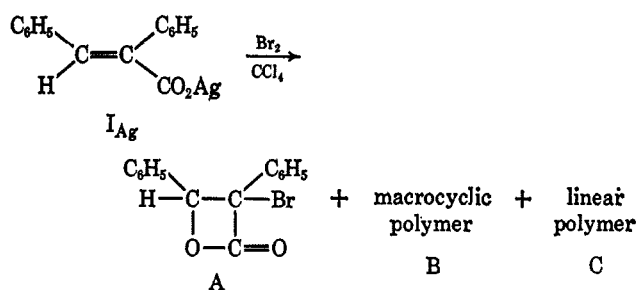
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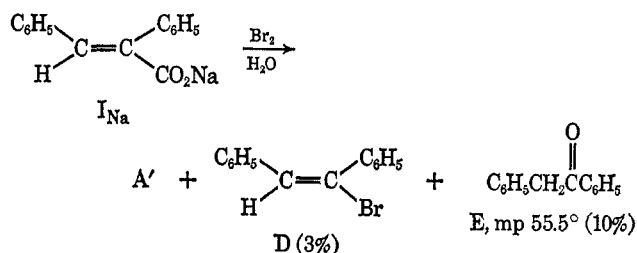
Received September 26, 1968

In 1957, Berman and Price² reported that sodium *cis*- and *trans*-stilbene- α -carboxylates were brominated to give good yields of the corresponding bromostilbenes. We have been unable to confirm this report, nor have others.^{3,4} Our further studies have, however, led to the isolation of bromo- β -lactone **A** and its macrocyclic (**B**) and linear polymer **C** which we wish to report here.

- (1) From the Ph.D. Dissertation of H. W. Blunt, 1965.
- (2) J. D. Berman and C. C. Price, *J. Amer. Chem. Soc.*, **79**, 5474 (1957).
- (3) B. B. Jarvis and W. Protz, Department of Chemistry, University of Maryland, College Park, Md.; *J. Org. Chem.*, **33**, 874 (1968).
- (4) W. Brown and S. Jankowski, Argonne National Laboratories, Argonne, Ill., private communication.



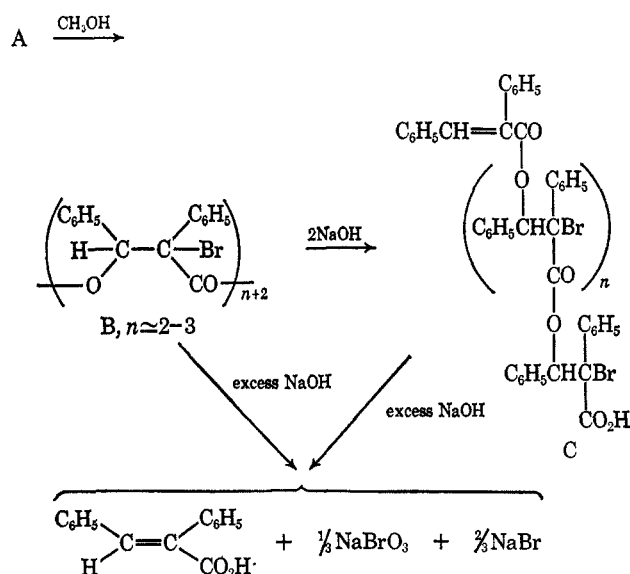
The product obtained from the sodium salt in water almost certainly included a β -lactone (ir absorbance at 1850 cm⁻¹) but it could not be separated by chromatography. Unlike β -lactone **A**, it failed to produce macrocyclic polymer **B** on warming in methanol, suggesting **A'** may be a geometric isomer of **A**.



The *trans* salts (**II_{Ag}** and **II_{Na}**) gave essentially the same results, except that *no* bromostilbene was isolated from **II_{Na}** and the recovered acid was **I**, not **II**.

The formation of a bromolactone is analogous to the similar reaction reported for dimethylmaleic acid.⁵ The lactone, readily identified by its ir absorbance at 1850 cm⁻¹, was obtained as an oil.

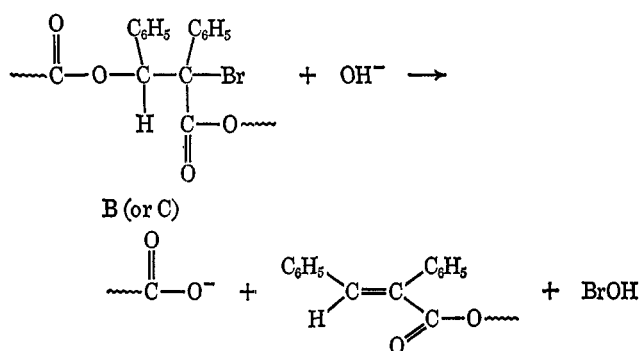
The macrocyclic polymer was readily converted into a linear polymer by 2 equiv of base. On more vigorous conditions, both polymers were degraded to **I** and sodium bromate,⁶ with consumption of 2 equiv of base per unit. The cleavage of any one of the ester links in **B** could occur more readily than further reaction of these links in **C** due to ring strain in **B**, more favorable



- (5) D. S. Tarbell and P. D. Bartlett, *J. Amer. Chem. Soc.*, **59**, 408 (1937).
- (6) A. G. Cotton and G. Wilkinson ["Advanced Inorganic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1962] report the equilibrium constant ($K = 10^{15}$) heavily favors disproportionation of hypobromite to bromate and bromide.

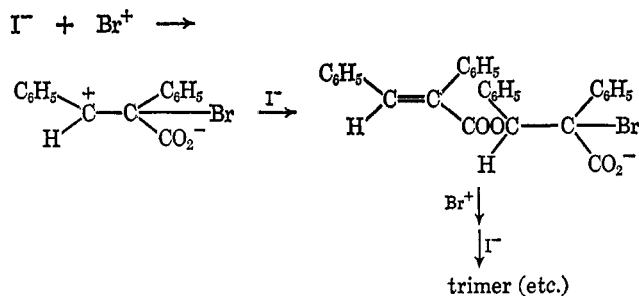
orientation in B, or the negative charge acquired by C in base.

So far as we are aware the elimination of the elements of hypobromous acid from a bromohydrin ester has not been previously reported. There are a number of features of the structures of B and C which would favor this course for the reaction in these cases. First of all, normal saponification of the ester would be highly sterically hindered since hydroxyl attack at the ester carbon expands this group to tetrahedral geometry, whereas attack on bromine could be linear with the C-Br bond and would certainly be further from the hindered site because of the larger radius of bromine than carbon. Second, an elimination reaction would be favored not only by relief of steric strain but by the resonance stabilization of the resulting double bond, conjugated to a carbonyl group and two phenyl groups. We therefore formulate the reaction as involving nucleophilic attack by base on bromine followed by (or concurrent with) loss of the β -carboxylate ion.⁷ It is



of interest to point out that this reaction occurred much more readily to open the ring in B than to degrade further the linear polymer C thus formed to I.

In addition to formation of linear polymer C by ring opening of macrocyclic lactone, it may be formed during bromination by the following sequence of reactions.



The various products had readily differentiated infrared spectra in the carbonyl frequency. The β -lactones, A and A', each had a strong sharp band at 1850 cm^{-1} . The macrocyclic polymer B was characterized by a strong band at 1760 cm^{-1} . The linear polymer C had

bands at 1750 (unconjugated) and 1720 cm^{-1} (conjugated) while the deoxybenzoin E had absorption at 1690 cm^{-1} .

In a study similar to ours on bromination of I_{Na} and II_{Na} in water, Jarvis and Protz⁸ obtained deoxybenzoin and *cis*- and *trans*-stilbenes, by glpc, in yields appreciably better than those which we obtained by column chromatography. They did not detect the β -lactone (A') which may have decarboxylated on heating to the stilbenes.

Experimental Section⁸

cis- and *trans*-stilbenecarboxylic acids were prepared by the method of Fieser.⁹ The silver salts were prepared as before,² dried under vacuum at $50\text{--}60^\circ$, and stored in a darkened desiccator. The carbon tetrachloride was dried over molecular sieves for 24 hr.

Bromination of I_{Ag} (10 g) dispersed in 300 ml of CCl_4 was accomplished by adding it and 5 g of Br_2 in 100 ml of CCl_4 to 500 ml of CCl_4 with stirring. After 3 hr the pale yellow mixture was filtered, washed with dilute sodium bisulfite, then with dilute sodium bicarbonate, and concentrated to 50 ml at $35\text{--}38^\circ$. The solution was charged to a $3.5 \times 20\text{ cm}$ column of Florisil. Elution with 250 ml of CCl_4 gave a mixture of A ($\nu_{\text{CO}} 1850\text{ cm}^{-1}$) and B ($\nu_{\text{CO}} 1760\text{ cm}^{-1}$), converted entirely into B, mp $125\text{--}132^\circ$, by dissolving in hot methanol.

Anal. Calcd for $(\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br})_n$: C, 59.42; H, 3.66; Br, 26.35. Found: C, 59.57; H, 3.78; Br, 26.58.

Elution with 250 ml of 3:1 benzene-methanol gave linear polymer C. Acidification of the bicarbonate wash precipitated I, mp $173\text{--}174^\circ$. Results of three experiments are summarized in Table I.

TABLE I
REACTION OF SILVER *cis*-STILBENECARBOXYLATE WITH BROMINE IN CCl_4

Expt	Amt, %				M_n of C	
	I	A	B	C	Titration ^a	Vapor osmtry ^b
1 ^a	20		26	12 ^d	1050	114
2 ^b	6	18	6	30 ^e	1330	1400
3 ^c	1	24	9	23 ^f	2430	2600

^a I_{Ag} air dried. ^b I_{Ag} vacuum dried at 50° for 48 hr. ^c Same as footnote b, then ground and redried for 25 hr additional. ^d *Anal.* Calcd for C ($n = 2$) (1134): C, 63.56; H, 4.00; Br, 21.15. Found: C, 63.41; H, 4.24; Br, 20.03. ^e *Anal.* Calcd for C ($n = 3$) (1436): C, 62.56; H, 3.90; Br, 22.35. Found: C, 61.98; H, 4.26; Br, 24.07. ^f *Anal.* Calcd for C ($n = 2 + \text{Br}_2$): C, 554.9; H, 3.39; Br, 31.26. Found: C, 56.03; H, 3.61; Br, 31.14. ^g By alkaline titration in DMSO, assuming two titratable acid groups. The titration and osmometric molecular weights would also be in agreement for one titratable acid group if the polymer molecules were dimeric in benzene (through association *via* carboxylic acid end groups). ^h By Mechrolab vapor osmometer in benzene.

One sample of linear polymer C (2.3 g) was fractionated from 200 ml of CCl_4 by adding 300 ml of methanol to precipitate 0.61 g of polymer, mp $168\text{--}233^\circ$. Removal of CCl_4 by evaporation and further methanol addition gave additional fractions of 0.42 g (mp $128\text{--}141^\circ$), 0.37 g (mp $105\text{--}129^\circ$), and 0.58 g (mp $95\text{--}115^\circ$), as well as 0.09 g of I (mp 172°). This "linear" polymer C showed broadened nmr absorption at $\delta 5.6$ and 6.8 ppm .

Bromination of II_{Ag} (15 g) with 7.5 g of bromine in 300 ml of CCl_4 for 3 hr at room temperature gave 1.1 g of I from the bicarbonate wash, 4.55 g of a mixture of A and B from CCl_4 elution of the Florisil column, and C from methanol-benzene elution.

(7) A similar nucleophilic attack on bromine in vicinal dibromide by benzhydryl anion has recently been suggested by W. C. Kofron and C. R. Hauser, *J. Amer. Chem. Soc.*, **90**, 4126 (1968).

(8) All melting points are uncorrected. Analyses were by Dr. A. Bernhardt, Max Planck Institute, West Germany.

(9) L. F. Fieser, *J. Chem. Educ.*, **31**, 293 (1954).

Purification of A.—A crude sample of 4.55 g of A was dissolved in 10 ml of warm CCl_4 and applied to the Florisil column. Elution with five 25-ml portions of low-boiling petroleum ether (bp 30–60°) gave 3.0 g of oil, ν_{CO} 1850 cm^{-1} , still containing a small amount of B (by ir): n_D^{20} 1.6124; d_4^{20} 0.833. It solidified to a glass at -70° and the nmr spectra showed sharp singlets at δ 5.95 and 7.10 ppm in the proper 10:1 ratio.

Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br}$: C, 59.42; H, 3.66; Br, 26.35. Found: C, 59.60; H, 3.34; Br, 26.30.

The molecular weight by vapor osmometer was 350 g/mol, compared with the calculated value of 303.

Conversion of A into B.—When a boiling solution of 2 g of A in 25 ml of methanol was chilled in a Dry Ice–acetone bath, a 1.8 g yield of B (mp 125–132°, ν_{CO} 1760 cm^{-1}) was obtained. The nmr spectra showed broadened singlets at δ 5.8 and 7.0 ppm in the proper ratio.

Anal. Calcd for $(\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br})_n$: C, 59.42; H, 3.66; Br, 26.35; mol wt, 1212. Found: C, 59.33; H, 3.80; Br, 26.49; mol wt, 1380.

The polymer was amorphous by X-ray diffraction.

Alkaline Titration of B.—While there was no evidence for acid end groups in B (from ir), samples in DMSO could be titrated with 0.21 *N* NaOH. Assuming conversion of B into C 2 mol of NaOH would be required. The observed molecular weight from titration was 1186, comparing favorably to the 1380 determined by vapor osmometry and the theoretical value for $n = 2$ of 1212. Acidification after titration precipitated 98% of the initial sample as C.

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{Br}_2$: C, 63.56; H, 4.00; Br, 21.15. Found: C, 63.57; H, 4.32; Br, 20.26.

Saponification of B and C.—Weighed samples of B (or C) were refluxed in 100 ml of 1 *N* ethanolic KOH for 40 hr. From back-titration with 1 *N* HCl, two samples of B were found to consume 2.02 and 2.00 equiv of NaOH per monomer unit. For C, 2.24 equiv of NaOH per monomer unit was consumed. After titration, addition of concentrated HCl precipitated I, mp 173–174°, in high yield.

The saponification mixture after refluxing contained a white crystalline precipitate. In one case, this material was collected by filtration, dissolved in water, and treated with KI and starch. Acidification produced a dark blue color. For two polymer samples, the precipitate was dissolved in water, acidified, treated with KI, and titrated with 0.1 *N* thiosulfate, showing 11.5 and 11% of the calculated titer. The ethanol filtrate when treated similarly showed only an additional 2.5%. Presumably the majority of the hypobromite was consumed by oxidizing the ethanol solvent, a reaction which can be used to prepare bromoform.

Bromination of I_{Na} was accomplished by dissolving 10 g of I and 1.6 g of NaOH in 200 ml of water followed by dropwise addition of 6.4 g of bromine with stirring at 50°. After cooling, the reaction mixture was extracted with three 100-ml portions of ether. The ether was washed with 1% sodium bisulfite then 2% alkali, 5% hydrochloric acid, and water. Drying and evaporation left 7.03 g of yellow oil, ν_{CO} 1850 and 1690 cm^{-1} . The ratio of A to E could be approximated from the ir spectrum and the elementary analysis of the mixture could then be rationalized on the basis of the composition indicated.

Anal. Calcd for 63.5% A, 14.1% D, 22.2% E: C, 66.08; H, 4.12; Br, 21.18. Found: C, 66.21; H, 4.42; Br, 21.16.

No separation was effected on Florisil, but on Woelm alumina (1.5 × 5 in) elution with petroleum ether (bp 30–60°) gave 0.32 g (3%) of D, identified by uv and ir spectra. Elution with CCl_4 gave 0.45 g (10%) of E (ν_{CO} 1690 cm^{-1} , mp 53–55°) after recrystallization from methanol. The lactone unfortunately could not be eluted from the alumina column.

Bromination of II_{Na} (10 g) similarly gave 1.12 g (25%) of E (from 4.6 g of crude neutral oil showing ν_{CO} 1850 and 1690 cm^{-1}). Acidification of the alkaline extract gave 2.0 g of I. Under conditions which completely converted the lactone A from silver salt into macrocyclic polymer B, the β -lactone (A') obtained from sodium salt bromination was stable in boiling methanol, yielding no precipitate on cooling, and leaving an oil on evaporation with the same ratio of ir absorption at 1850 and 1690 cm^{-1} as before heating in methanol.

Registry No.—I_{Ag}, 19926-54-6; I_{Na}, 15352-96-2; II_{Ag}, 19926-56-8; II_{Na}, 15352-97-3; A, 19926-34-2; C, 19926-35-3.

Enol Esters. IX.¹ The Use of Isopropenyl Esters as Acylation Agents. A Convenient Synthesis of Acyl Fluoride

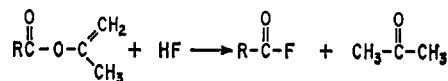
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Isopropenyl stearate, I, the stearylated enol of acetone, is a versatile stearylating agent. Its high degree of acylation activity is very probably associated with the ease of its thermal cleavage¹ to hexadecylketene. In preceding papers,^{1,3} we have described the synthesis of this reactive reagent and have detailed its use in the acylation of amides, imides, and several other compounds. We have now found further examples of the general utility of isopropenyl stearate taken as an example of an enol ester and would like here to present our findings. As will be seen below the reactions are general enol ester reactions and not limited solely to isopropenyl stearate.

When a stream of hydrogen fluoride is passed into an isopropenyl ester (whether neat or in solution in dry



ether) acetone is liberated leaving behind a residue, or a solution of, acyl fluoride. This acid fluoride synthesis was carried out in four aliphatic examples chosen for variation in chain length using isopropenyl acetate, octanoate, octadecanoate, and azelate esters. The acylated products are formed cleanly in high yield. The method offers advantages over the procedure of Olah and Kuhn,^{4a} who found that, when they used anhydrides as starting materials, only those derived from C_2 or C_3 acids reacted with hydrogen fluoride fast enough at hydrogen fluoride reflux temperature for preparative utility. These authors prefer to use acid chlorides at -10 to $+5^\circ$. The present procedure for acyl fluoride preparation does not require the intermediary preparation of acid chloride,^{4b} but it should be noted that, if desired for other purposes, acyl chlorides may be similarly prepared uncontaminated by reagents used in their preparation by using hydrogen chloride gas in place of hydrogen fluoride. This acyl chloride synthesis compares well⁵ with existing literature procedures using phosphorus trichloride, thionyl chloride,⁶ or oxalyl chloride⁷ in simplicity of operation, in yield, and particularly in purity of product.

(1) For the previous paper in this series, see E. S. Rothman, *J. Amer. Oil Chem. Soc.*, **45**, 189 (1968).

(2) Agricultural Research Service, U. S. Department of Agriculture.

(3) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).

(4) (a) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **82**, 2380 (1960); *J. Org. Chem.*, **26**, 237 (1961). (b) F. Seel and J. Langer, *Chem. Ber.*, **91**, 2553 (1958).

(5) Because of the importance to the food industry we anticipate that isopropenyl stearate will become a commercially available bulk chemical.

(6) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1658 (1959).

(7) H. E. Kenney, G. Maerker, and E. T. Donahue, *J. Amer. Oil Chem. Soc.*, in press.