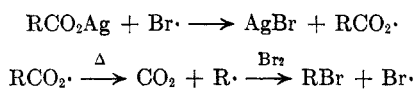


Reaction of Bromine with Silver Salts of Some Unsaturated Acids

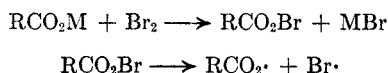
JOSEPH D. BERMAN¹ AND CHARLES C. PRICE²

Received May 31, 1957

It has been proposed³ that the Hunsdiecker reaction proceeds through a free-radical mechanism and some evidence has been advanced in support of such a course for the reaction.⁴



Berr⁵ has suggested an alternate scheme involving radicals.



An earlier claim⁶ that optical activity was retained in the transformation of (+)-2-phenylpropionate to (+)-1-phenethyl bromide is contrary to other evidence on the stereochemistry of the Hunsdiecker reaction,^{5,7} and it has been reported that it cannot be duplicated.^{5,8}

In view of the greater configurational stability of trivalent nitrogen and of carbanions when incorporated at a double bond, we have investigated the reaction of silver salts of *cis*- and *trans*-forms of two α,β -unsaturated acids, cinnamic and stilbene- α -carboxylic acids, to see whether any additional evidence could be obtained concerning the steric course of the Hunsdiecker reaction.

In accord with earlier observations on saturated acids^{5,7,8} the intermediates in the bromination of silver *cis*- and *trans*- α -cinnamates are evidently configurationally unstable as indicated by the fact that the β -bromostyrene produced was exclusively the *trans*-isomer. The fact that the melting point was two or three degrees low is probably due to the contamination with β -chlorostyrene, since qualitative analysis proved the presence of chlorine (absent in commercial β -bromostyrene by the same test).

(1) Department of Chemistry, Harpur College, Endicott, N. Y.

(2) Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

(3) C. C. Price, *Reactions at the Carbon-Carbon Double Bond*, Interscience Publishers, New York, 1946.

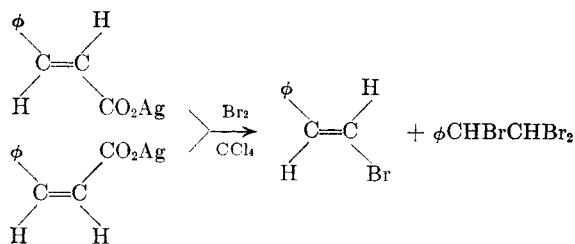
(4) See R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

(5) C. E. Berr, doctoral dissertation, University of California, Los Angeles, 1952.

(6) C. L. Arcus, A. Campbell, and J. Kenyon, *J. Chem. Soc.*, 1510 (1949).

(7) (a) R. T. Arnold and P. Morgan, *J. Am. Chem. Soc.* **70**, 4248 (1948); (b) F. Bell and I. F. B. Smyth, *J. Chem. Soc.*, 2372 (1949); (c) M. Heintzeler, *Ann.*, **569**, 102 (1950).

(8) J. Cason, M. J. Kalm, and R. H. Mills, *J. Org. Chem.*, **18**, 1670 (1953); D. C. Abbott and C. L. Arcus, *J. Chem. Soc.*, 3195 (1952).



The presence of chlorine supports the earlier reports that carbon tetrachloride could participate in the reaction.^{5,7c,9} Both the stereochemistry and the incorporation of chlorine are readily explained by the free radical mechanism.⁴

Silver *cis*- and *trans*-stilbene- α -carboxylate also gave the same product, but it was, surprisingly, a polymer containing little or no halogen. Its analysis, degradation by alkali and infrared spectrum suggest it is a polyester, formed by condensation of an active intermediate with carbonate ion used in the work-up of the product. The identity of infrared spectra for the polymers from the two acids at least suggests that the course of the reaction does not involve preservation of the stereochemical identity at the unsaturated carbon atoms. The structure of this polymer and the mechanism of its formation are being studied further.

Silver *p*-methoxyphenylacetate gave an intractable tarry resin, but the *m*-methoxy isomer gave an 80% yield of 2-bromo-5-methoxyphenylacetic acid.

EXPERIMENTAL

The acids were prepared as described earlier.¹⁰ The silver salts were prepared by treating an aqueous solution of the sodium salt with an equivalent of aqueous silver nitrate. If the first precipitate was dark, it was removed by filtration before adding the remaining silver nitrate. The white or cream colored precipitate was collected, washed thoroughly with water, with methanol and ether, and dried thoroughly in a vacuum at 80° before use.

Silver *trans*-cinnamate (12.6 g., 0.05 mole) in 200 ml. of dry carbon tetrachloride was treated with 8 g. of bromine, added slowly to the refluxing solution. After 30 min., the mixture was cooled, filtered, washed with aqueous sodium carbonate, and dried. Distillation of the latter gave 1.6 g. (17.5%) of *trans*- β -bromostyrene, b.p. 69° (1.5 mm.), n_D^{20} 1.6086, m.p. 3–4.5° (lit.¹¹ n_D^{20} 1.6094, m.p. 6–7°) and 6 g. (35%) of β -bromostyrene dibromide, b.p. 134–135° (2 mm.) m.p. 35–37° (lit.¹¹ m.p. 37–38°). A gummy residue (1.2 g.) was left in the still pot. Acidification of the carbonate extract gave 0.6 g. (8%) of the original acid, identified by melting point (131.5–133°) and mixture melting point.

A qualitative test for chlorine¹² on the β -bromostyrene was positive while the same test on a commercial sample was negative.

(9) R. A. Barnes and R. J. Proschka, *J. Am. Chem. Soc.*, **72**, 3188 (1950); W. G. Dauben and H. Tilles, *J. Am. Chem. Soc.*, 3185 (1950); P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **75**, 5370 (1953).

(10) J. D. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5474 (1957).

(11) R. Fittig and F. Bender, *Ann.*, **195**, 142 (1879).

(12) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, John Wiley and Sons, New York (1948) p. 57.

A similar reaction at room temperature gave 1 g. (11%) of *trans*- β -bromostyrene, 2.5 g. (15%) of β -bromostyrene dibromide, 0.5 g. (7%) of parent acid, and 2.4 g. of undistillable residue. The β -bromostyrene contained some chlorine.

Silver *cis*-cinnamate (6 g., 0.03 mole) was similarly treated with bromine in boiling carbon tetrachloride to produce 0.4 g. (10%) of *trans*- β -bromostyrene, b.p. 55–57° (0.6 mm.), m.p. 4–5°, 2.2 g. (25%) of β -bromostyrene dibromide, 2.1 g. of tarry, resinous residue, and 0.4 g. (12%) of parent acid, identified by melting point (63–64°) and mixture melting point.

Silver *cis*-stilbene- α -carboxylate (17 g., 0.05 mole) in 250 ml. of dry boiling carbon tetrachloride was treated with bromine and worked up as before. From the carbonate wash water, 1.7 g. of starting acid, m.p. 169–171°, was obtained. Evaporation of the carbon tetrachloride left 7.2 g. of viscous oil, free of bromine by qualitative analysis. Addition of this oil to methanol gave a white solid of indeterminate melting point with infrared spectrum similar to the original oil, both showing strong carbonyl peaks at 5.75 and 5.88 μ .

Anal. Calcd. for $(C_{16}H_{12}O_5)_x$: C, 67.61; H, 4.22; Mol. wt., 1420. Found: C, 67.68; H, 4.58; Mol. wt. 1405 (Rast.).

The polymeric oil dissolved in boiling aqueous potassium hydroxide. No neutral fraction could be isolated. Acidification precipitated 0.8 g. of the parent acid, m.p. 169–171°.

Similar reactions carried out in cold carbon tetrachloride and in benzene at room temperature and at the boiling point gave the same material in about the same yield.

Silver *trans*-stilbene- α -carboxylate (8.3 g., 0.025 mole) was treated in the same way producing 7 g. of viscous oil and 0.6 g. of original acid, m.p. 134–136°. The oil gave a white precipitate in methanol or ethanol with the same properties as from the *cis*-acid. Sodium fusion indicated no halogen and the infrared spectra of the two materials were identical.

Silver *p*-methoxyphenylacetate (9 g., 0.033 mole) was treated with bromine in boiling carbon tetrachloride and worked up as above. From the carbonate wash, 1.2 g. (23%) of original acid was recovered. Distillation of the carbon tetrachloride residue gave no material corresponding to the benzyl bromide or alcohol and left 2.5 g. of neutral, tarry, bromine containing resin.

The *m*-methoxy isomer was similarly brominated. After filtering off the silver bromide, crystals appeared in the carbon tetrachloride so it was evaporated, leaving a crystalline solid entirely soluble in sodium bicarbonate. Acidification gave 10 g. (82%) of *2-bromo-5-methoxyphenylacetic acid*, m.p. 112–115°. Recrystallization from acetone and from water sharpened the melting point to 114–115° (lit. 115°) neutral equivalent, 241, 244 (calcd. 245).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, IND.

4'-Nitro-2-stilbenol

W. E. SOLODAR AND M. GREEN

Received May 31, 1957

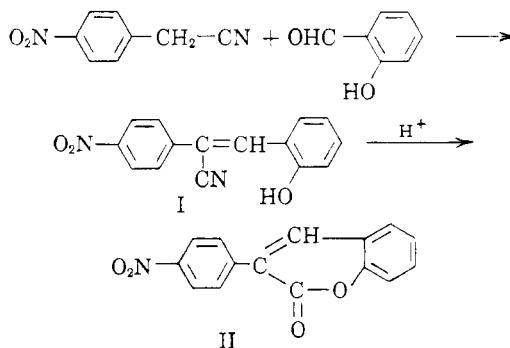
The only previously reported synthesis of 4'-nitro-2-stilbenol¹ is that of Merckx.² He attempted to prepare it by condensing *p*-nitrophenylacetonitrile and salicylaldehyde, followed by acid hydrolysis

(1) Cullinane (ref. 5), in his preparation of II, obtained an oily by-product which he acetylated to obtain 4-nitro-2'-acetoxystilbene.

(2) R. Merckx, *Bull. soc. chim. Belges*, **58**, 460 (1949).

of the resulting *o*-hydroxy-2-phenylcinnamionitrile (I). These reactions have been repeated in our laboratories and the product of acid hydrolysis of I shown to be 3-*p*-nitrophenyl coumarin (II), rather than the desired 4'-nitro-2-stilbenol.

Our product, a yellow crystalline material melting at 260° (Merckx reported 257°), was insoluble in alkali and was recovered unchanged after treatment with acetic anhydride, a lack of reactivity inconsistent with that expected if the compound were the stilbenol and contained an ortho phenolic group. Analysis indicated the empirical formula $C_{15}H_9NO_4$, as contrasted with $C_{14}H_{11}NO_3$, the formula of the desired stilbenol.



The ready tendency of *o*-hydroxy- α -phenylcinnamionitriles and of *o*-hydroxy- α -phenylcinnamic acids to form coumarins is well known.^{3–6} An authentic sample of II was prepared from *p*-nitrophenylacetic acid and salicylaldehyde,⁵ and gave no melting point depression on admixture with our product. Merckx's "4'-nitro-2-stilbenol," therefore, is 3-*p*-nitrophenylcoumarin. The observation by Merckx that "saponification" of the nitrile occurs only in those cyanostilbenes prepared from salicylaldehydes (*i.e.*, having an ortho hydroxyl available to form a six-membered ring) is thus explained as coumarin formation. Similarly, the anomalously melting 2',4'-dinitro-2-stilbenol^{7,8} reported by Merckx must be assumed to be 3-(2',4'-dinitrophenyl)-coumarin.

We have prepared 4'-nitro-2-stilbenol by demethylation of the known 4-nitro-2'-methoxystilbene.⁹ The stilbenol thus prepared is an alkali-soluble, dark yellow microcrystalline solid. Acetylation with acetyl chloride gave the acetyl ester.⁵

(3) W. Borsche and F. Streitberger, *Ber.*, **37**, 3163 (1904).

(4) T. Kiewiet and H. Stephens, *J. Chem. Soc.*, 639 (1931).

(5) N. M. Cullinane, *J. Chem. Soc.*, 123, 2053 (1923).

(6) N. P. Buu-Hoi and D. Lavit, *J. Org. Chem.*, **21**, 21 (1956).

(7) P. Ruggli and O. Schmid, *Helv. Chim. Acta*, **18**, 253 (1935).

(8) J. M. Gulland and R. Robinson, *J. Chem. Soc.*, 127, 1493 (1925).

(9) P. Pfeiffer, *Ber.*, **48**, 1795 (1915).