

## Preparation of the Esters

The acetates were prepared by heating the carbinols with acetic anhydride at 160–170° for three hours, the propionates with propionic anhydride at 180–190° for three hours. The butyrates were prepared by heating with butyryl chloride at 120–130° for three hours.

The usual procedure of the Schotten–Baumann reaction was used in preparing the benzoates with benzoyl chloride. The benzoate of trichloromethyl-*o*-phenylcarbinol was also prepared by heating with benzoic anhydride at 230–235° for three hours, but this resulted in excessive decomposition in the case of the tribromo compound.

ESTERS OF TRICHLOROMETHYL-*o*-CHLOROPHENYLCARBINOL

	Formula	Analyses for Cl, %		B. p., °C.	Mm.	M. p., °C.	$d_{20}^{20}$
		Calcd.	Found				
1 Acetate	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> Cl <sub>4</sub>	46.98	47.04	162–163	4	86	...
2 Propionate	C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>4</sub>	44.89	44.74	175	4	38	...
3 Butyrate	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> Cl <sub>4</sub>	42.99	43.13	201	15	..	1.363
4 Benzoate	C <sub>15</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>4</sub>	38.98	39.20	.....	..	81	...

The acetate and propionate crystallize slowly on standing at room temperature for several weeks. The benzoate was recrystallized from 95% alcohol.

ESTERS OF TRIBROMOMETHYL-*o*-CHLOROPHENYLCARBINOL

	Formula	Chlorine, %		Bromine, %		B. p., °C.	Mm.	M. p., °C.	$d_{20}^{20}$
		Calcd.	Found	Calcd.	Found				
1 Acetate	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> ClBr <sub>3</sub>	8.14	8.28	55.08	55.19	102–103	...	...	...
2 Propionate	C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> ClBr <sub>3</sub>	7.89	7.97	53.36	53.19	78	...	...	...
3 Butyrate	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> ClBr <sub>3</sub>	7.67	7.76	51.86	51.97	208–210	4	.....	1.803
4 Benzoate	C <sub>15</sub> H <sub>10</sub> O <sub>2</sub> ClBr <sub>3</sub>	7.13	7.39	48.21	48.37	.....	...	91	...

The acetate was recrystallized from 75% acetic acid, the propionate and benzoate from 95% alcohol.

The average yield of all these esters was 85%.

All of the esters are insoluble in water and readily soluble in carbon bisulfide, benzene, acetone, ether, chloroform and carbon tetrachloride.

The butyrates are readily soluble in 95% ethyl alcohol and methyl alcohol, while the acetates, propionates and benzoates are only sparingly soluble in these solvents.

## Summary

Trichloromethyl-*o*-chlorophenylcarbinol and tribromomethyl-*o*-chlorophenylcarbinol as well as their acetic, propionic, butyric and benzoic esters have been prepared and studied.

MISSOULA, MONTANA RECEIVED DECEMBER 17, 1934

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## A Total Asymmetric Synthesis by Addition of Bromine to an Ethylenic Linkage

BY TENNEY L. DAVIS AND ROBERT HEGGIE

Partial asymmetric syntheses, in which a molecule containing an asymmetric atom is taken at the beginning and additional asymmetry is found in the product, have now been reported in considerable number.<sup>1</sup> Asymmetric decompositions have been reported by Kuhn and Braun,<sup>2</sup> Kuhn and Knopf,<sup>3</sup> and Mitchell.<sup>4</sup> Souty<sup>5</sup> has recently found that the rate of mutarotation of certain sugars is different in right and in left circularly polarized light of wave length 5461 Å. but not different in right and in left circularly polarized light of wave length 5890 Å. A number of unsuccessful attempts to add bromine asymmetri-

cally to the ethylenic linkage have been recorded.<sup>6</sup> So far as we are aware, the only total asymmetric synthesis, starting from optically inert materials, which has been reported heretofore is that of Karagunis and Drikes,<sup>7</sup> who procured optically active products by the addition of chlorine to triarylmethyl radicals in circularly polarized light of wave lengths 4300 and 5890 Å.

We now wish to report the production of optically active trinitrostilbene dibromide by the addition of bromine to 2,4,6-trinitrostilbene in circularly polarized light of wave length 3600–4500 Å. This reaction has seemed to us to be particularly well suited to the purpose of asymmetric synthesis in visible light, for the reasons that the

(1) Ritchie, "Asymmetric Synthesis and Asymmetric Induction," Oxford, 1933, Part I, Chapters II and III.

(2) Kuhn and Braun, *Naturwissenschaften*, **17**, 227–228 (1929).

(3) Kuhn and Knopf, *ibid.*, **18**, 183 (1930); *Z. physik. Chem.*, **7B**, 292–310 (1930).

(4) Mitchell, *J. Chem. Soc.*, 1829–1834 (1930).

(5) Souty, *Compt. rend.*, **199**, 198–199 (1934).

(6) Ritchie, *loc. cit.*, Part I, Chapter IV; cf. Mitchell, "The Cotton Effect and Related Phenomena," London, 1933.

(7) Karagunis and Drikes, *Naturwissenschaften*, **21**, 697 (1933); *Nature*, **132**, 354 (1933).

dark reaction is negligible, that trinitrostilbene is yellow in color, possessing an absorption band in the violet, and finally that trinitrostilbene, having a phenyl and a trinitrophenyl group which differ markedly from one another in their electrical character, might be expected to contain a semi-polar ethylenic linkage.

The absolute value of the rotation which we have been able to secure reproducibly ( $0.04^\circ$ ) is very small, but well beyond the limit of error of the polariscope which was employed. Two impartial observers in this Laboratory have independently confirmed our observation that optical activity is actually produced. Bromine has strong absorption for light of the wave length which we have used, excited bromine atoms being formed and a chain reaction initiated<sup>8</sup> in which the activated trinitrostilbene molecules may or may not take part. Since optical activity can be produced only by reaction of excited trinitrostilbene molecules, it follows that the concurrent absorption of the light by the bromine materially decreases its effect. Kuhn and Knopf<sup>8</sup> calculated the expected rotation after 40% decomposition in the case of the asymmetric photochemical decomposition of  $\alpha$ -azidopropionic dimethylamide, where the quantum yield is one, to be  $1.25^\circ$ . If we assume the same rotation and anisotropy factor to hold in our case—a poor assumption, but as good as we can make while lacking knowledge of these constants—then we should expect only one-thirtieth of this rotation, or about  $0.04^\circ$ , if the quantum yield is thirty.

We have carried out in circularly polarized light the addition of bromine to trinitrostilbene in carbon tetrachloride, in benzene, in glacial acetic acid, and in nitrobenzene solution, and have obtained optically active products in each case. Nitrobenzene was found to be most suitable because of its greater solvent power, and because it gave the most consistent results. In every case the reaction mixture assumed an optical activity which increased to a maximum and then decreased slowly and finally disappeared altogether as the reaction proceeded to completion. When the optically active material was removed from the beam of polarized light and allowed to stand in diffuse daylight, it also lost its activity.

No optically active material is formed by the addition of bromine to trinitrostilbene in diffuse daylight or in unpolarized light of wave length

3600–4500 Å. Optically inactive trinitrostilbene dibromide is not rendered active by exposure in nitrobenzene solution to circularly polarized light of wave length 3600–4500 Å. for periods of time equal to those in which optically active products were produced from bromine and trinitrostilbene.

The production of optically active trinitrostilbene dibromide in our experiments indicates that the ethylenic linkage of trinitrostilbene is by no means the rigid structure conceived by van't Hoff and suggests that it is in some manner potentially asymmetric. Our results give support to the hypothesis of asymmetric induction advanced by Erlenmeyer and developed by such recent authors as Lowry, Phillips, McKenzie and Ritchie<sup>1</sup> (Part II) to explain the complex rotatory dispersion of esters of optically active alcohols and of  $\alpha$ -ketonic esters, and certain phenomena of mutarotation.

Our polarized light was right circularly polarized, in which respect it was similar to the right circularly polarized light which predominates at the earth's surface in reflected sunlight. Kuhn's<sup>2,3</sup> work has shown that optically active substances in nature may arise from the directing influence of circularly polarized light in the asymmetric decomposition of racemic mixtures. The present<sup>4</sup> results suggest that they may be produced by direct synthesis.

In continuing this investigation, we plan to study the absorption spectra of trinitrostilbene and trinitrostilbene dibromide, to work with other additive reagents as well as bromine, and to try the effect of circularly polarized monochromatic light of various wave lengths.

## Experiments

The apparatus used for the production of circularly polarized light was a modification of that employed by Coker and Thompson<sup>9</sup> and Dailey and Benedict.<sup>10</sup> Light from a glass-enclosed mercury arc was rendered approximately monochromatic (3600–4500 Å.) by a filter of blue cobalt glass, then circularly polarized by reflection at the polarizing angle from a plate of black glass and by passage through a thin sheet of mica. In our first experiments the solutions were irradiated in glass crystallizing dishes, in the later ones in a glass cell  $1.5 \times 1.5 \times 2.5$  cm.

**Solubility of Trinitrostilbene.**—One hundred cc. of carbon tetrachloride at  $20^\circ$  dissolves about 0.40 g. of trinitrostilbene, 100 cc. of glacial acetic acid about 0.86 g., 100 cc. of benzene about 5 g., and 100 cc. of nitrobenzene 12 to 14 g.

(9) Coker and Thompson, *Engineering*, **19**, 134 (1912).

(10) Dailey and Benedict, *This Journal*, **51**, 808 (1929).

(8) Mecke, *Trans. Faraday Soc.*, **27**, 359–375 (1931).

**Trinitrostilbene Dibromide.**—Two and one-half grams of trinitrostilbene was dissolved in 50 cc. of benzene, 1.5 g. of bromine added, and the solution allowed to stand for eight hours in the light of a 250-watt electric light. Spontaneous evaporation yielded a light yellow crystalline product melting at 164–170°. This material dissolved in boiling glacial acetic acid, but the solution turned reddish and finally reddish-brown. Recrystallization from glacial acetic acid yielded pure trinitrostilbene dibromide, white needles, melting at 177.5–179° with the liberation of bromine. The yield, 56% of the theoretical, could easily be improved. When a sample of the white material was kept in a test-tube in the laboratory, it was found that the portions of it which were next to the glass, and most exposed to the action of light, turned yellow and liberated bromine. Bromine was determined by boiling samples of the substance with alcoholic sodium iodide solution and titrating the iodine which was liberated. Found: bromine, 32.7, 33.6; calculated, 33.7.

**Irradiation Experiments.**—A saturated solution of trinitrostilbene in carbon tetrachloride was treated with bromine and exposed to circularly polarized light in a glass crystallizing dish. After eleven hours a portion of the liquid examined in a 5-cm. polariscope tube showed a rotation of 0.019°, after twenty-four hours 0.021°. When the residual liquid was exposed to daylight on the window ledge, the bromine color disappeared and the material was found to be without optical activity.

A solution of 2.5 g. of trinitrostilbene and 1.5 g. of bromine in 50 cc. of benzene was similarly exposed to polarized light. Portions were removed from time to time, diluted with twice their volume of benzene to increase their transparency, and examined in the 5-cm. polariscope tube. The observed rotatory powers of the diluted solutions were—after thirty minutes 0.019°, after ninety minutes 0.022°, after 315 minutes 0.023°, and after 1335 minutes 0.078°.<sup>11</sup> In a similar experiment with a different sample of benzene the maximum observed rotation was 0.017°, while another experiment in which 0.6 g. of bromine was used instead of 1.5 g. gave a maximum observed rotation of 0.023°. Attempts to increase the transparency of the solutions by removing the bromine with thiosulfate resulted in the complete loss of optical activity. The experimentation with benzene solutions was not carried further, and no attempt was made to secure more consistent results, for it was judged more profitable to work with solvents in which trinitrostilbene is more readily soluble.

Five cc. of glacial acetic acid containing 0.043 g. of trinitrostilbene and three drops of bromine was exposed to circularly polarized light in a small glass cell of cross section 1.5 × 1.5 cm., and measurements of the rotatory

(11) At some time between the third and fourth observation the mercury arc lamp broke. Hence, the duration of the exposure reported as 1335 minutes is really not known accurately.

power of the solution were made from time to time directly upon the cell, with results as follows—after seventy minutes 0.017°, after 127 minutes 0.014°, after 177 minutes 0.022° and after 427 minutes 0.008°.

In other experiments the trinitrostilbene was dissolved in carefully purified nitrobenzene, 2 to 4 drops of bromine was added, and the irradiations and measurement of optical activity were made in the small glass cell as before. The results are indicated in Table I.

TABLE I

CHANGE OF OPTICAL ACTIVITY WITH DURATION OF EXPOSURE TO POLARIZED LIGHT IN NITROBENZENE SOLUTION

Expt. Trinitrostilbene, g. Nitrobenzene, cc.	I 0.200 3		II 0.500 5		III 0.847 5	
	Time, min.	Obsd. rot.	Time, min.	Obsd. rot.	Time, min.	Obsd. rot.
	0	0.000	0	0.000	0	0.000
	110	.030	30	.036	30	.012
	245	.032	60	.031	63	.021
	1435	.036	95	.034	112	.029
	1615	.020	390	.040	156	.015
	2770	.013	1300	.014	824	.009
			4130	.000		

Trinitrostilbene and bromine were dissolved together in nitrobenzene, the solutions were exposed to polarized light, and aliquot portions were removed at regular intervals and titrated for bromine with thiosulfate in order to determine the velocity of the reaction. First and second order constants were calculated, but the results were unsatisfactory—the constants of both orders being about ten times as large at the beginnings as at the ends of the experiments.

### Summary

Bromine combines with trinitrostilbene in carbon tetrachloride, in glacial acetic acid, and in nitrobenzene solution in a beam of right circularly polarized light of wave length 3600–4500 Å. to form an optically active (dextrorotatory) product.

The product on standing, whether in ordinary or in polarized light, loses its optical activity, and the activity is not restored by further exposure to polarized light. We infer that the optical activity which we have observed arises therefore at the moment of the synthesis of the compound.

Trinitrostilbene dibromide is unstable, decomposing with the liberation of bromine slowly in daylight at ordinary temperatures and rapidly when melted.

The investigation is being continued.

CAMBRIDGE, MASS.

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