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Asymmetric Synthesis. II. Addition of Chlorine to Trinitrostilbene

BY TENNEY L. DAVIS AND ROBERT HEGGIE

In continuing the work which was described in an earlier paper,[1] we find that bromine does not combine with trinitrostilbene in a beam of circularly polarized sodium light of wave length 5890–5896 Å. to yield a product which is optically active. A solution of trinitrostilbene in nitrobenzene does not absorb sodium light, asymmetric molecules of trinitrostilbene if present in the liquid are not activated, and the result is entirely as would be expected.

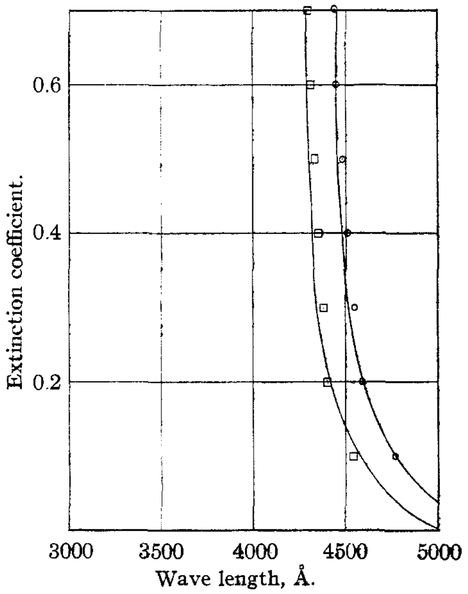

Fig. 1.—Absorption spectra: □, nitrobenzene; ○, trinitrostilbene in nitrobenzene.

Trinitrostilbene was allowed to combine with chlorine in a beam of circularly polarized light of wave length 3600–4500 Å., and was found to yield an optically active product. Nitrobenzene was used as a solvent, and the apparatus was the same as that which had been used in the earlier experiments with bromine. It was hoped that the smaller absorption of chlorine would result in the activation of a greater number of trinitrostilbene molecules and in the production of a greater optical activity. The observed optical activity, however, was about the same as in the experiments with bromine, a result which indicates that the greater quantum yield in the reaction with chlorine had nullified the advantage of the lessened absorption.

The reaction with chlorine is much faster than with bromine; maximum rotations were obtained in about forty-five minutes whereas several hours had been necessary in order to obtain maximum rotations in the experiments with bromine. Further exposure to the polarized light caused a gradual disappearance of the optical activity. The maximum observed rotation was 0.034° when the measurements were made with yellow light of wave length 5890 Å., and 0.050° when they were made with green light of wave length 5461 Å.

It was found that racemization of the optically active trinitrostilbene dichloride was fairly rapid in green light, so that, while it was in general possible to make a measurement of the rotation first in yellow light and then in the green, it was not feasible to carry out the operations in the reverse order.

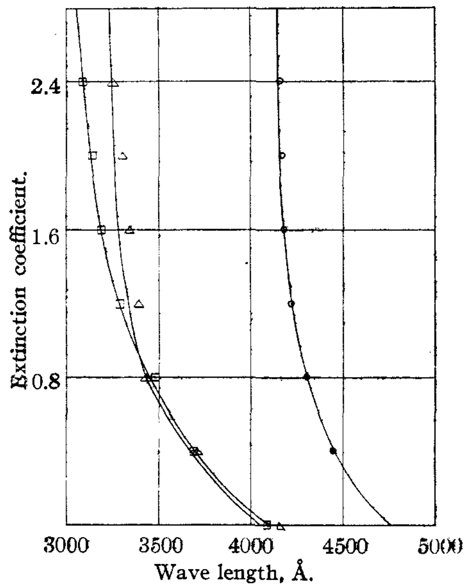

Fig. 2.—Absorption spectra in glacial acetic acid solutions: ○, trinitrostilbene; □, trinitrostilbene dichloride; △, trinitrostilbene dibromide.

The absorption spectra of nitrobenzene, of trinitrostilbene in nitrobenzene, of trinitrostilbene and its dichloride and dibromide in glacial acetic

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[1] Davis and Heggie, THIS JOURNAL, **57**, 377 (1935).

acid, and the transmission of the cobalt blue glass plate which was used have been determined in order to gain a definite idea of the region of the spectrum effective in these experiments. The results are indicated in Figs. 1, 2 and 3. They show that of the important mercury lines only those of wave lengths 4341, 4348 and 4360 Å. are transmitted both by the cobalt glass and the nitrobenzene in the cell, and that these three lines are transmitted only 7, 8 and 8.5%, respectively. The nitrobenzene acts as an efficient filter, absorbing completely all of the mercury lines of wave length less than these three. Since the dichloride and dibromide of trinitrostilbene do not absorb in this region, it follows that the optical activity which was obtained cannot have been produced by their asymmetric decomposition—a conclusion which agrees with the experimental fact, reported earlier, that optically inactive trinitrostilbene dibromide is not rendered optically active by exposure to polarized light.

Trinitrostilbene dichloride, like the dibromide, decomposes spontaneously, more rapidly in the light than in the dark, with the liberation of halogen.

Experiments

Addition of Bromine to Trinitrostilbene in Circularly Polarized Sodium Light.—The apparatus was the same as that described in the earlier paper, except that the source of light was a General Electric Company sodium lab-arc, CT No. NA-160-6SCI. In each experiment 0.347 g. of trinitrostilbene together with an equimolecular amount of bromine was dissolved in 5 cc. of nitrobenzene, and the solution was irradiated in a 1.5 × 1.5 × 2.5 cm. glass cell. The cell was removed from time to time and polarimetric measurements were made directly upon it. The results of a typical experiment, shown in Table I, indicate that no optical activity was produced; in fact they serve very well to illustrate the degree of reproducibility of the zero reading on the polarimeter.

TABLE I

EFFECT OF CIRCULARLY POLARIZED SODIUM LIGHT

Time, minutes	Polarimeter reading
60	0.004 ± 0.005°
135	.004 ± .008°
180	.004 ± .009°
240	− .006 ± .006°
300	.002 ± .006°
420	− .002 ± .006°
540	.004 ± .008°
660	.000 ± .008°
1440	− .002 ± .007°
4320	.002 ± .004°

Addition of Chlorine to Trinitrostilbene in Circularly Polarized Light of Wave Length 3600–4500 Å.—The apparatus was the same as that described in the earlier paper. Three-tenths of a gram of trinitrostilbene and an equimolecular quantity of chlorine were dissolved in 5 cc. of nitrobenzene and irradiated in the small glass cell. The cell was removed from time to time and polarimetric measurements were made directly upon it, with yellow sodium light and in a few cases also with green light of wave length 5461 Å. The results of five experiments are shown in Table II.

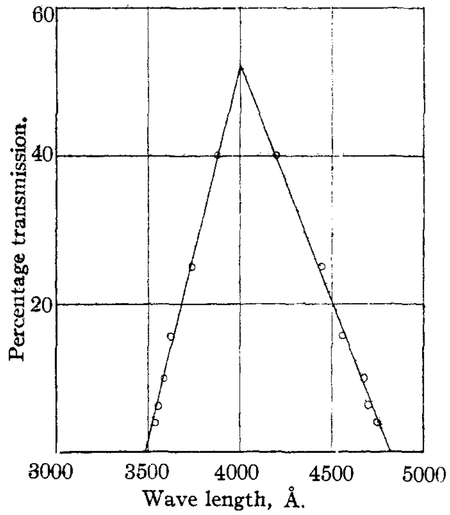

Fig. 3.—Light transmission by cobalt blue glass plate.

TABLE II

EFFECT OF CIRCULARLY POLARIZED LIGHT OF WAVE LENGTH 3600–4500 Å.

Experiment	Time, minutes	Polarimeter readings Yellow: l = 5890 Å.	Green: l = 5461 Å.
1	25	0.016 ± 0.003°	
	45	.028 ± .003°	
	73	.012 ± .003°	
	100	.012 ± .003°	
	125	.012 ± .004°	
	147	.014 ± .003°	
	1309	.006 ± .002°	
2	23	.011 ± .002°	
	45	.027 ± .003°	
	75	.014 ± .003°	
	157	.010 ± .002°	
	217	.006 ± .002°	
	4344	.004 ± .002°	
3	34	.014 ± .002°	
	67	.018 ± .002°	
	224	.008 ± .002°	
	1174	.004 ± .002°	
4	45	.034 ± .002°	0.050 ± 0.002°
5	46	.031 ± .004°	.045 ± .003°

Racemization during Polarimetric Measurements.—After one forty-five minute run, the rotatory power of the material in the cell was measured with lights of various wave lengths, in the order indicated, with results as follows: 5209 Å., 0.038°; 5461 Å., 0.028°; 5890 Å., 0.000°; 6101 Å., 0.004°; 6438 Å., −0.002°. The measurements were made in the reverse order on the material from another forty-five minute run, with results: 6438 Å., 0.018°; 6104 Å., 0.024°; 5890 Å., 0.028°; 5461 Å., 0.029°; 5209 Å., 0.024°.

Preparation of Trinitrostilbene Dichloride.—Three grams of trinitrostilbene was dissolved in a solution of chlorine in benzene and exposed to the radiation from a 250-watt lamp for two days. The residue from the evaporation of the benzene solution, recrystallized from glacial acetic acid, yielded 1.5 g. of the pure dichloride, white crystals, m. p. 185.5–186.5° (corr.) with slight decomposition. The material was analyzed by refluxing a sample with an alcohol solution of sodium iodide, and titrating the liberated iodine. Calcd. for $C_{14}H_9O_6N_3Cl_2$, 18.4%. Found: Cl, 18.5, 18.6%. The precipitate which remained after the titration, recrystallized from glacial acetic acid, yielded pure trinitrostilbene, m. p. 156.5–158°, identified by mixed melting point with a known sample.

Summary

In circularly polarized sodium light of wave length 5890–5896 Å., trinitrostilbene does not combine with bromine to yield an optically active product. Trinitrostilbene does not absorb light of this wave length.

Trinitrostilbene combines with chlorine in circularly polarized light of wave length 3600–4500 Å. to yield optically active trinitrostilbene dichloride. The reaction with chlorine is more rapid than with bromine, the maximum rotatory power being attained in about forty-five minutes. On longer irradiation, the optical activity decreases and finally disappears.

The absorption spectra of trinitrostilbene and its dichloride and dibromide have been measured.

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The Catalytic Interconversion of Ortho–Para Hydrogen over Iron, Platinum and Nickel Catalysts

By P. H. Emmett and R. W. Harkness

In previous communications[1,2,3] a few of the results that have been obtained in a study of the catalytic interconversion of ortho to para hydrogen over iron synthetic ammonia catalysts have been presented. The present paper gives the detailed experimental results together with a discussion of their relation to other published catalytic ortho–para interconversion measurements. The conversion over nickel and platinum catalysts has been studied only in so far as it is poisoned by the activated adsorption of hydrogen.

Experimental

The ortho–para hydrogen conversion apparatus was similar to that described by Bonhoeffer and Harteck.[4] Tank hydrogen containing 0.2% or less nitrogen as an impurity was freed from oxygen by passage over hot finely divided copper, and passed through a flowmeter, a phosphoric anhydride drying tube and a well baked out charcoal trap of 100-cc. capacity immersed in liquid air. This charcoal tube served the double purpose of removing the small amount of nitrogen that was in the hydrogen and of acting as a catalyst for bringing the initial ortho–para ratio to that corresponding to the temperature of liquid air. The hydrogen could then be passed either directly from the charcoal bulb through a U-tube immersed in liquid air and into the catalyst tube, or through a tube of platinized asbestos heated to 200°, a U-tube immersed in liquid air, and into the catalyst tube. Samples of the gas could be taken from the exit of the catalyst tube into a conductivity gage of the type already described.[4] Readings were taken with a pressure of 40 mm. in the gage; the latter was operated in such a way as to keep the current through the platinum filament constant. The temperature of the liquid air bath surrounding the gage and of that around the charcoal tube were taken with a 10-junction copper-constantan couple in conjunction with a Leeds and Northrup type K potentiometer. Corrections were applied to the gage reading for any temperature changes in the temperature of the liquid air bath. The maximum combined uncertainties of each analysis of the ortho–para mixture corresponded to about 2% of the difference in the gage resistance for normal 3:1 ortho–para compared to 1:1 ortho–para hydrogen.

The doubly promoted iron synthetic ammonia catalyst (931) contained 1.59% potassium oxide and 1.3% aluminum oxide as promoters. The preparation, reduction, and properties of this type of catalyst have been described many times previously.[5] The pure iron catalyst (973) contained 0.15% aluminum oxide as impurity. The nickel catalyst was made by reducing a fused oxide in

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[1] Emmett and Harkness, This Journal, **54**, 403 (1932).

[2] Harkness and Emmett, *ibid.*, **55**, 3496 (1933).

[3] Harkness and Emmett, *ibid.*, **56**, 490 (1934). The principal results of adsorption measurements made in conjunction with the ortho–para conversion studies were also reported in this communication. The detailed account of these adsorption studies is, for convenience, being published separately from the ortho–para work.

[4] Bonhoeffer and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

[5] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).