TABLE III

Temp., °K.	ΔS[5] Equilib. data	ΔS 3rd law	ΔS Free rot.	ΔS Rest. rot.
457	27.44	28.39	25.34	28.39
475	27.56	28.37	25.40	28.37
491	27.73	28.35	25.47	28.35

$\Delta H^\circ_{355} = 13{,}400$ cal.[6]

culated using free rotation and the third law entropies, since the equilibrium data show the latter to be correct.

Kemp and Pitzer have demonstrated this for ethane and courageously predicted the discrepancies in other cases. *We agree with these authors that there is no reason to doubt the practical applicability of the Third Law.*

(5) Parks and Kelley, *J. Phys. Chem.*, **32**, 734 (1928).

(6) We wish to thank Professor G. B. Kistiakowsky for advance notice on this recently published value.

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
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S. C. SCHUMANN
J. G. ASTON

RECEIVED FEBRUARY 23, 1938

HYDROGEN FLUORIDE AS A CONDENSING AGENT

Sir:

We have found that anhydrous hydrogen fluoride will promote the reaction between either olefins and benzene or aliphatic halides and benzene. The following reactions have been accomplished and others are in progress. We are continuing the work with other aromatic compounds.

All reactions were run in the liquid phase at 0° with stirring. The time required varied from two to twenty-four hours. Varying amounts of hydrogen fluoride were used without changing the results.

1. From the reaction of propylene and benzene two products were isolated. The one present in larger amount boiled at 149–150° at 730 mm., and gave an acetamino derivative that melted at 105–105.5°. Isopropylbenzene boils at 152° at 758 mm. and its acetamino derivative melts at 106°.

2. Isopropyl chloride gave indications of a reaction. Some material that boiled above 150° was produced. This formed an acetamino derivative, m. p. 166°, which may be the derivative of diisopropylbenzene.

3. Isobutylene formed two products. One was a liquid, b. p. 166.5–168° at 728 mm., the other was a crystalline solid, m. p. 77–78°. *t*-Butylbenzene boils at 168–170° at 760 mm. and di-*t*-butylbenzene melts at 78°.

4. *t*-Butyl chloride gave two products; one a liquid, b. p. 167–170°, and the other a solid, m. p. 77°. A mixed melting point of this solid and that formed in (3) was 76.5–77.5°. An acetamino derivative of the liquid melted at 169–170°. A dinitro derivative of the solid melted at 188°. The known acetamino derivative of *t*-butylbenzene melts at 170° and the dinitro derivative of di-*t*-butylbenzene melts at 191°.

5. Trimethylethylene formed two products, b. p. 188° and 262–265°.

6. *t*-Amyl chloride formed the same two products that were found in the reaction of trimethylethylene.

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 8, 1938

THE PREPARATION AND PHOTOCHEMICAL OXIDATION OF 2,4-CHOLESTADIENE

Sir:

A further study of the method of preparation of 2,4-cholestadiene [H. E. Staveley and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937)] indicates that for consistent results it is desirable to use alumina which has been freshly reactivated by heating in a shallow pan at 200° for four hours. Activated Alumina, Grade A, 40 to 80 mesh (Aluminum Ore Co., East St. Louis, Ill.) is suitable. It is convenient to carry out the reaction in a small Pyrex retort. The preliminary heating should be continued for at least thirty minutes beyond the time when the droplets refluxing from the sides fail to crystallize when cooled locally by a jet of compressed air. Subsequent distillation yields 60 to 70% of a product having a specific rotation +90–100°. Distillation at higher temperatures (higher pressures) than previously recommended leads to the formation of cholesterilene, m. p. 79.5–80°, $[\alpha]^{20}\text{D}$ −51.4° in ether.

The isolation and purification of the 2,4-cholestadiene has been achieved by systematic fractional recrystallization from small amounts of ether. This is carried out in centrifugal filtration tubes [E. L. Skau, *J. Phys. Chem.*, **33**, 951 (1929); E. L. Skau and L. F. Rowe, *Ind. Eng. Chem., Anal. Ed.*, **3**, 147 (1931)] the yields being kept high by centrifuging at −78°. By this means a pure product is obtained, m. p. 68.5°, $[\alpha]^{23}\text{D}$ + 168.5° in ether (30% yield from cholesterol). Comparison of the absorption spectrum and spe-