

the most accurate measurements) must be regarded as being compatible with theory.

### Summary

The chain transfer theory of modifier action has been tested on commercial GR-S by means of molecular weight and sulfur content determina-

tions. The number of sulfur atoms per molecule was found to range between 0.7 and 1.1, to be compared to the theoretical value of unity. In view of the experimental difficulties involved, the results are considered to be in good agreement with the theory.

URBANA, ILLINOIS

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[CONTRIBUTION FROM PURDUE UNIVERSITY AND PURDUE RESEARCH FOUNDATION]

## The Nitration of Bicyclo[2,2,1]heptane<sup>1</sup>

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In connection with work in this Laboratory on the mechanism of the vapor-phase nitration reaction, bicyclo[2,2,1]heptane was treated with nitric acid in the vapor phase in order to determine whether or not a bridgehead carbon atom would be nitrated under these conditions. Nametkin and co-workers reported that liquid-phase nitration of camphane yields no tertiary derivative.<sup>2</sup>

**Procedure.**—The hydrocarbon was synthesized by the method of Joshel and Butz as improved by Thomas.<sup>3</sup> A vapor-phase nitration using 100 g. of it dissolved in 200 ml. of carbon tetrachloride for convenience of handling, was made with 1:1 ratio of nitric acid at 400–410° and atmospheric pressure.<sup>4</sup> The nitro derivatives were separated from the unreacted materials by fractional distillation at reduced pressure, stirred over 10% aqueous sodium hydroxide for 30 hours, extracted with ether and the ether extract, after the ether had evaporated, purified by fractional

crystallization and chromatography in ether solution over Norite. The resulting solid, somewhat waxy like its parent hydrocarbon, melted sharply at 63°; yield about 50% of nitrated product. Tested with the indicator developed by Davidson,<sup>5</sup> it was found to contain no primary or secondary nitro group. It is therefore 1-nitrobicyclo[2,2,1]heptane.

*Anal.* Calcd. for C<sub>7</sub>H<sub>11</sub>NO<sub>2</sub>: C, 59.55; H, 7.86; N, 9.92. Found: C, 59.05; H, 7.9; N, 9.66.

This proves the possibility of nitrating a bridgehead carbon atom.

The secondary nitro derivatives were regenerated by carbon dioxide, but not separated and identified.

Sincere appreciation is extended to the Purdue Research Foundation and Mr. J. K. Lilly for the financial support which made this research possible.

### Summary

1-Nitrobicyclo[2,2,1]heptane has been prepared by the vapor-phase nitration of bicyclo[2,2,1]heptane, proving the possibility of nitrating a bridgehead carbon atom.

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(1) An abstract of the thesis by R. T. Blickenstaff, submitted to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, February, 1946.

(2) Nametkin, Dobrovolskaya and Oparina, *J. Russ. Phys.-Chem. Soc.*, **47**, 405, 409 (1915).

(3) Joshel and Butz, *THIS JOURNAL*, **63**, 3350 (1941); Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

(4) For a reference to the general technic employed, see Seigle and Hass, *Ind. Eng. Chem.*, **31**, 648-650 (1939).

(5) Davidson, *J. Chem. Education*, **19**, 154, 532 (1942).