viscosity and hydrocarbon type for any of the elastomer-solvent combinations. Specifically, there is no indication of consistently lower relative viscosities with aromatic thinners, as Reynolds found with natural rubber solutions.

This does not rule out the probability of varying degrees of aggregation of synthetic rubbers in these solvents, since Doty, Wagner, and Singer (*2*) demonstrated that molecular association is possible without significant increase in viscosity. They concluded that there was molecular association of poly(vinyl chloride) (0.25 to 1.0%) solutions in dioxane at various temperatures because eightfold decrease was observed in weight-average molecular weight with increase in temperature from 25° to 60° C., although the specific viscosity ($\eta/\eta_0 - 1$) was practically unchanged in that temperature range. From these results they concluded that the molecules in the associated clusters are so tightly coiled and packed that the viscosity is reduced to almost the same value as the unassociated molecules at the same concentration.

ACKNOWLEDGMENT

The author is grateful to Ralph Burns, a summer student from Laval University, and to C.F. Acton and W.D. Horley, Research Department technicians, for carrying out the experimental work and plotting viscosity data; and to Polymer Corp., Sarnia, Canada, and Esso Research and Engineering Co. for supplying samples of various synthetic rubbers.

LITERATURE CITED

(1) Burrell, H., *Offic. Dig. Federation Soc. Paint Technol.* **27**, No. 369, 726 (1955).
(2) Doty, P., Wagner, H., Singer, S., *J. Phys. Colloid Chem.* **51**, 32 (1947).
(3) King L.F., *Offic. Dig. Federation Soc. Paint Technol.* **35**, No. 457, 144 (1963); **37**, No. 482, 302 (1965).
(4) Reynolds, W.W., Gebhart, H.J., J. CHEM. ENG. DATA **5**, 220 (1960).
(5) Reynolds, W.W., Gebhart, H.J., *Offic. Dig. Federation Soc. Paint Technol.* **29**, No. 394, 1174 (1957).
(6) Streeter, D.J., Boyer, R.F., *Ind. Eng. Chem.* **43**, 1790 (1951).

RECEIVED for review June 24, 1965. Accepted December 7, 1965.

---

# Rearrangement

## The Composition of Cycloalkenes and Alcohols Produced by Demjanov Rearrangement of Cyclohexanemethylamine

RYOTARO KOTANI
Research Laboratory, Kureha Spinning Company, Ltd., Takatsuki, Osaka, Japan

**Denjanov rearrangement of cyclohexanemethylamine was reinvestigated, yielding as products 1-methylcyclohexene (10.2%), 3-methylcyclohexene (0.9%), methylenecyclohexane (7.9%), cycloheptene (5.4%), 1-methylcyclohexanol (17.9%), 2-methylcyclohexanol (1.2%), cyclohexanemethanol (14.8%), and cycloheptanol (24.3%). The composition of the product was determined by gas chromatography and NMR spectroscopy.**

DURING an investigation (*4*) of rearrangements in cyclohexane series, it became necessary to know the composition of cycloalkenes produced by Demjanov rearrangement of cyclohexanemethylamine. Although a few groups of workers (*7, 8, 9*) have investigated this reaction, there is a lack of data for the cycloalkene composition in spite of its relatively high yield.

Each component in the cycloalkene mixture from cyclohexanemethylamine was separated by preparative scale gas chromatography and identified by comparison of its retention time and NMR spectrum with those of an authentic sample. Quantitative analysis of the cycloalkene mixture by NMR spectroscopy was in good agreement with that obtained by gas chromatography as shown in Table I. Examination of the alcohol fraction from the amine by gas chromatography revealed the presence of 2-methylcyclohexanol in addition to the three isomeric alcohols reported by Smith and Baer (*8*), but its configuration remained unidentified. NMR analysis failed to detect this alcohol, however. 1-Methylcyclohexanol was formed in much higher amounts than reported by Smith and Baer—17.9% instead of 2%.

Table I. Products Produced by Demjanov Rearrangement of Cyclohexanemethylamine

| | Yield, % | |
|---|---|---|
| | Gas chromatography | NMR spectroscopy |
| 1-Methylcyclohexene | 10.2 | 9.7 |
| 3-Methylcyclohexene | 0.9 | 1.2 |
| Methylenecyclohexane | 7.9 | 8.2 |
| Cycloheptene | 5.4 | 5.3 |
| Total (cycloalkenes) | 24.4 | 24.4 |
| 1-Methylcyclohexanol | 17.9 | 19.5 |
| 2-Methylcyclohexanol$^a$ | 1.2 | ... |
| Cyclohexanemethanol | 14.8 | 13.3 |
| Cycloheptanol | 24.3 | 25.4 |
| Total (alcohols) | 58.2 | 58.2 |

$^a$The configuration remained unidentified.

## EXPERIMENTAL

All melting points and boiling points are uncorrected.

**Product Analysis.** Gas chromatographic analysis was carried out on a Yanagimoto GCG-2 gas chromatograph, equipped with a 500 × 0.35 cm. column packed with 80- to 100-mesh Celite which was coated with the appropriate stationary phase. The stationary phases employed were: 30% by weight of a 40% solution of silver nitrate in tetraethylene glycol, used for cycloalkenes at 60° C.; 30% by weight of Apiezon grease L, used for alcohols at 150° C. Helium outlet flow rates were 45 and 60 cc. per minute, respectively. Peak areas were determined by half-width and peak height measurements. No correction was made for slight differences in the thermal conductivity cell response of the isomeric compounds.

NMR analysis was run at 25° C. for cycloalkenes and at 70° C. for alcohols in carbon tetrachloride (5–10%) on a Varian Associates Model V-4311 high-resolution spectrometer operating at 60 Mc. with tetramethylsilane ($\tau$10.00) as an internal standard. The chemical shifts (in $\tau$-value) and resonance line shapes used for structural assignment were: 1-methylcyclohexene (a multiplet, 4.71, an olefinic proton; an incompletely resolved doublet, 8.40, methyl protons), 3-methylcyclohexene (a complex multiplet, three main lines, 4.44, 4.47, and 4.53, olefinic protons; an asymmetrical doublet, 9.00 and 9.11, apparent coupling constant $J$ = 6.6 c.p.s., methyl protons), methylenecyclohexane (a quintet, 5.47, terminal methylene protons), cycloheptene (a triplet, 4.30, $J$ = 3.7 c.p.s., olefinic protons), 1-methylcyclohexanol (a singlet, 8.85 methyl protons), cyclohexanemethanol (a 1 to 1 doublet, 6.66, methylene protons of the —$CH_2OH$), and cycloheptanol (a broad absorption, 6.25, a methine proton). Areas under absorption bands were determined by an electric integrator.

**Materials.** The reference compounds used in gas chromatographic and NMR analyses were prepared as follows: 1-Methylcyclohexene, b.p. 110° C.; 3-methylcyclohexene, b.p. 103° C.; methylenecyclohexane, b.p. 102° C.; and cycloheptene, b.p. 115° C., were prepared according to the procedures of Mosher (*6*), Hückel and Hubele (*3*), Turner and Garner (*10*), and Willstätter (*11*), respectively. All the above cycloalkenes were purified by preparative scale gas chromatography and their structures were proved by NMR spectroscopy. 1-Methylcyclohexanol, b.p. 68° C. (20 mm.); cyclohexanemethanol, b.p. 91–92° C. (18 mm.); cycloheptanol, b.p. 184–185° C., were prepared following the procedures of Mosher (*6*), Gilman and Catlin (*2*), and Matthews and Becker (*5*), respectively. A mixture of *cis*- and *trans*-2-methylcyclohexanol was commercially available, but these isomers could not be resolved by gas chromatography under the experimental conditions employed.

Cyclohexanecarboxamide, m.p. 184–185° C., and cyclohexanemethylamine, b.p. 74° C. (35 mm.) were prepared by the procedure of Baumgarten, Bower, and Okamoto (*1*).

**Demjanov Rearrangement of Cyclohexanemethylamine.** Cyclohexanemethylamine (45.2 grams, 0.4 mole) was treated with sodium nitrite in dilute aqueous orthophosphoric acid at room temperature for 1 hour and then at 95° C. for 1 hour according to the procedure of Kotani (*4*) for 1-methylcyclohexanemethylamine. Fractional distillation of the crude product gave 9.4 grams of the cycloalkene mixture, b.p. 90–115° C., and 26.6 grams of the alcohol mixture, b.p. 50°–95° C. (20 mm.), leaving 1.0 gram of a high boiling substance. This may be a nitrogen-containing compound which often appears in Demjanov reactions, but no attempt was made to identify it.

## ACKNOWLEDGMENT

The author expresses his deep gratitude to C. D. Hurd of Northwestern University for his unfailing guidance, and to Takashi Kobayashi for his continuing interest. The author is also indebted to Shiro Satoh for NMR studies and to Tadashi Ikegami for his technical assistance.

## LITERATURE CITED

(1) Baumgarten, H.E., Bower, F.A., Okamoto, T.T., *J. Am. Chem. Soc.* **79**, 3145 (1957).
(2) Gilman, H., Catlin, W.E., "Organic Syntheses," 2nd ed., Coll. Vol. **I**, p. 188, Wiley, New York, 1961.
(3) Hückel, W., Hubele, A., *Ann.* **613**, 27 (1958).
(4) Kotani, R., *J. Org. Chem.* **30**, 350 (1965).
(5) Matthews, D.N., Becker, E.I., *Ibid.*, **21**, 1317 (1956).
(6) Mosher, W.A., *J. Am. Chem. Soc.* **62**, 552 (1940).
(7) Ruzicka, L., Brugger, W., *Helv. Chim. Acta* **9**, 399 (1926).
(8) Smith. P.A.S., Baer, D.R., *J. Am. Chem. Soc.* **74**, 6135 (1952).
(9) Smith, P.A.S., Baer, D.R., "Organic Reactions," Vol. **11**, p. 157, Wiley, New York, 1960.
(10) Turner, R.B., Garner, R.H., *J. Am. Chem. Soc.* **80**, 1424 (1958).
(11) Willstätter, R., *Ann.* **317**, 221 (1901).

RECEIVED for review June 28, 1965. Accepted November 15, 1965.