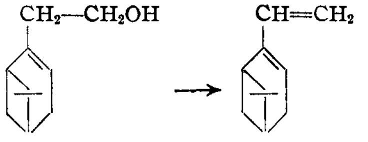

to the allylic methylene group.[1] The allylic methinyl hydrogen atom in nopadiene would not be expected to retard because it occurs on a bridgehead carbon atom.[2]

Nopadiene derived from the *l*-nopinene of gum turpentine is optically active and presumably is pure levo isomer.

In the color test for conjugated unsaturation with *p*-nitrobenzenediazonium chloride reagent,[3] nopadiene gave a strong positive test. Several other dienes and terpenes were tested for comparison. Most of the dienes gave positive tests. Terpenes having a tendency to isomerize to monocyclics containing conjugated systems under acid conditions, such as the pinenes, gave delayed positive tests.

Experimental

Nopol was obtained from the Glidden Company, Jacksonville, Florida, and was prepared from commercial β-pinene (nopinene) from the same source, by the autoclave method.[4] The nopol had the properties, b.p. 135–136°, n^{25}_D 1.4918 (lit. 1.4920), and α^{23}_D $-35.7°$ (10-cm. tube) (lit., α^{25}_D $-35.5°$).

A mixture of 77 g. (0.46 mole) of nopol, 20 g. (0.36 mole) of potassium hydroxide, 0.5 g. of phenyl-β-naphthylamine, and 150 g. of diethyleneglycol diethyl ether was refluxed under a fractionating column containing Raschig rings. During three hours 210 g. of distillate boiling in the range 98–185° was collected. After the distillate was washed thoroughly with water there remained 52 g. (75% yield) of nopadiene, n^{24}_D 1.5044.

In a similar experiment with tetraethyleneglycol dimethyl ether as diluent the reflux was carried out under vacuum. The yield of nopadiene was 50%.

When 166 g. (one mole) of nopol was dehydrated with 5.6 g. of potassium hydroxide with no diluent present, the distillate contained 16 g. of water and 15 g. (10% yield) of crude nopadiene. The material in the still-pot was separated from catalyst and distilled, giving 31 g. of distillate boiling up to 183° (3 mm.); the undistilled portion was a solid resin when cool.

A sample of nopadiene purified by distillation through a column (glass helices; 28 theor. plates) had the following properties: b.p. 179° (738 mm.); b.p. 85.5–86.5° (30 mm.); d^{25}_4 0.8842; n^{25}_D 1.5044; α^{23}_D $-30.16°$ (10 cm. tube).

Molecular refraction: Calcd. for $C_{11}H_{16}$: 47.66 (D). Found: 49.69 (D). Exaltation: +2.03. An exaltation of +0.48 has been assigned to the cyclobutane ring of the pinene ring system.[5] The remaining exaltation, +1.55, is due to conjugation, comparing with an exaltation of +1.67 due to conjugation in 2,4-hexadiene.[6]

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.89. Found: C, 88.61; H, 11.01.

Test for Conjugated Unsaturation.—The materials which were tested were purified by distillation. Tests were carried out in acetic acid–dioxane solution with *p*-nitrobenzenediazonium chloride in acetic acid, according to the directions of Fieser and Campbell.[7] A positive test was formation of an orange or red color which was more pronounced after five minutes than immediately after addition of the reagent.

Nopadiene and alloöcimene gave immediate red colorations, and 2-methylpentadiene, 2,3-dimethylbutadiene and myrcene, orange colorations, which were darker in color in 15 minutes. Isoprene, piperylene, naphthalene, nopol, terpinolene and dipentene gave weak tests, the colorations being unchanged light yellow at first and amber or orange within five minutes. The tests on α-pinene and nopinene showed no color change in five minutes, but had turned from light yellow to orange within 15 minutes. Chloroprene gave a negative test, remaining light yellow after 15 minutes.

Polymerization Tests.—A test-tube containing a few ml. of nopadiene and a granule of benzoyl peroxide was placed under a General Electric RS sunlamp. After 40 hours it was a sticky yellow polymer. Nopadiene without benzoyl peroxide, similarly exposed, was yellow in color and still fluid.

Sealed tubes each containing 7 g. of nopadiene and a few granules of benzoyl peroxide under carbon dioxide were ovenaged at 85°. After 160 hours contents of a tube containing nopadiene was still liquid, as was the contents of a tube containing equal amounts of methyl methacrylate and nopadiene. A third tube containing methyl methacrylate and benzoyl peroxide without nopadiene contained solid polymer within 15 hours.

Bottles were charged with water 100, sodium lauryl sulfate 0.2, ammonium persulfate 0.2, sodium bicarbonate 0.4 and monomer 25.0 parts; after being flushed with carbon dioxide and capped, the bottles were placed in a 50° polymerizer. After 19.5 hours, a bottle containing acrylonitrile alone as monomer was filled with a stiff paste of polyacrylonitrile; from a bottle charged with 1:1 acrylonitrile and nopadiene, four grams of pasty polymer resembling polyacrylonitrile was isolated; and from a third bottle, charged only with nopadiene as monomer, was recovered 24 g. (96%) of nearly pure nopadiene, n^{25}_D 1.5048.

A bottle charged with 180 parts (72 g.) of water along with stearic acid 4.63, sodium hydroxide 0.67, potassium persulfate 0.30, modifier ($C_{12}H_{25}SH$) 0.6, butadiene 75 and nopadiene 25 parts was agitated in a 50° polymerizer. After 66 hours it contained 33.5 g. of copolymer and a considerable amount of unreacted butadiene. This represented a monomer conversion of 76%, the theoretical yield of copolymer being 40 g. Coagulated with aluminum sulfate (phenyl-β-naphthylamine present) and dried, the polymer had good milling characteristics.

Acknowledgment.—The writer wishes to acknowledge the assistance of Mr. E. F. Kluchesky, who carried out the emulsion polymerization experiments.

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[1] R. L. Frank, J. R. Blegen, G. E. Inskeep and P. V. Smith, *Ind. Eng. Chem.*, **39**, 893 (1947).

[2] R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *ibid.*, **39**, 890 (1947).

[3] K. H. Meyer, *Ber.*, **52**, 1468 (1919).

[4] J. P. Bain, THIS JOURNAL, **68**, 638 (1946).

[5] R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins, *ibid.*, **64**, 2978 (1942).

[6] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 677.

[7] L. F. Fieser and W. P. Campbell, THIS JOURNAL, **60**, 168 (1938).

The Beckmann Rearrangement of O-Picrylbenzophenone Oxime[1]

BY B. B. LAMPERT AND F. G. BORDWELL

By their kinetic studies of the rearrangement of O-picrylbenzophenone oximes and related compounds Chapman and co-workers[2] contributed greatly to our understanding of the Beckman rearrangement. They represented their rearrangements, carried out in anhydrous inert solvents, as shown for O-picrylbenzophenone oxime (I).

In view of their isolation of N-picrylbenzanilide (III), Chapman and Howis[2a] suggested that the previously reported[3] rearrangement of O-benzene-

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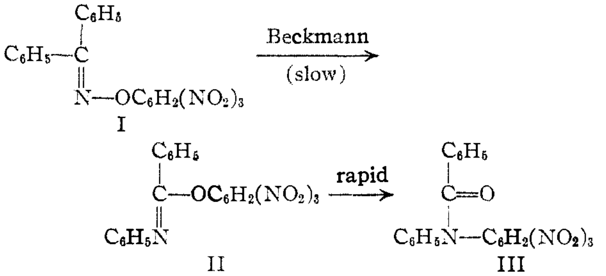
[1] The work was supported by the Office of Naval Research under Contract No. N7-onr-45007.

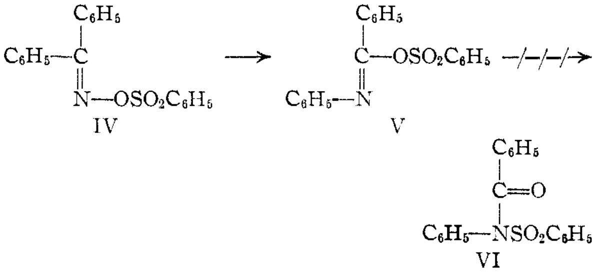
[2] (a) Chapman and Howis, *J. Chem. Soc.*, 806 (1933); (b) Chapman, *ibid.*, 1550 (1934); Chapman, *ibid.*, 1223 (1935); Chapman and Fidler, *ibid.*, 448 (1936).

[3] Kuhara, Matsumiya and Matsunami, *Mem. Coll. Sci. Kyoto*, **1**, 25 (1914).

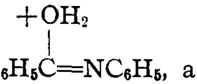


I II III

sulfonylbenzophenone oxime (IV) on standing or melting (m.p. 62°) probably had taken a similar course, and that the product, therefore, should be given structure VI rather than V, which had been assigned by Kuhara, *et al.*[3] Since Kuhara, *et al.*, reported that their product *hydrolyzed rapidly* to benzanilide and benzenesulfonic acid on addition of water, Chapman and Howis[2a] apparently were assuming this behavior for VI, and by implication for III. Despite the fact that N-benzoylbenzenesulfonamides similar to VI have long been known to be unreactive toward water,[4] this suggestion of Chapman and Howis has been accepted in several reviews of the Beckmann rearrangement.[5] Recently Oxley and Short[6] have presented additional convincing evidence showing that Kuhara's intermediate has structure V rather than VI.



IV V VI

To clarify the situation further we have shown that N-picrylbenzanilide (III) is not readily hydrolyzed by water. When the rearrangement of I was carried out in aqueous acetone solution the Beckmann product, benzanilide, was formed instead of III. If II is formed under these conditions, it must, like V, react rapidly with water to give benzanilide. Actually, in anhydrous media there is no compelling evidence to indicate that the transformation of I to III involves a Beckmann rearrangement, since the intermediate II has not been isolated. It seems probable, however, by analogy with the rearrangement of IV that the transformation I → II → III suggested by Chapman and Howis[2a] does take place. On the other hand, in aqueous acetone solution the solvolysis of the picryl group by water and attack by water at the doubly bonded carbon of I may be simultaneous with the migration of the phenyl group. This concerted process could give rise to an iminocarbonium ion,[7]  $C_6H_5\overset{+OH_2}{C}{=}NC_6H_5$, and benzanilide could be formed under these conditions without the intermediate formation of II.[8]

Experimental

Following the procedure of Chapman and Howis,[2a] O-picrylbenzophenone oxime (I) was prepared by adding 51 ml. of 0.5 *N* aqueous sodium hydroxide and 6.3 g. of picryl chloride alternately in small portions to a solution of 5.0 g. of benzophenone oxime in 50 ml. of acetone. When the resulting heterogeneous mixture was heated to the boiling point, a solid was formed, which proved to be a mixture of benzanilide and N-picrylbenzanilide (III). In a second experiment sufficient acetone was used in the preparation to keep I in solution. The solution was warmed on an electric hot-plate and aliquots of water introduced, taking care that no oil separated. When the solution reached about 50% concentration, acetone was boiled off until oil droplets appeared, and a seed crystal of benzanilide added. The solid obtained on cooling was separated and crystallized from benzene to yield 2.9 g. (58%) of benzanilide, m.p. and mixed m.p. 158–159°.

When a solution of 1 g. of III in 25 ml. of acetone and 10 ml. of water was refluxed for two hours, the recovery of starting material was quantitative.

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(4) See, for example, Gerhardt and Chiozza, *Ann. chim. phys.*, [3] **46**, 151 (1856); Wolkowa, *Z. Chem.*, 579 (1870); or note the slow hydrolysis of saccharin, Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 623.

(5) Jones, *Chem. Revs.*, **35**, 335 (1944); Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, 1945, p. 191. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 72, 75.

(6) Oxley and Short, *J. Chem. Soc.*, 1514 (1948).

(7) Jones, *Nature*, **157**, 519 (1946); Smith, THIS JOURNAL, **70**, 371 (1948); Harvill, Roberts and Herbst, *J. Org. Chem.*, **15**, 58 (1950).

(8) This possibility also exists, of course, for the hydrolysis or ammonolysis[6] of the O-benzenesulfonyl oximes.

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Purity Determination with the Electron Microscope

BY MAX A. LAUFFER[1]

An important and extremely difficult problem in the chemistry of proteins and other substances with large molecules is the determination of purity. The methods in current use, such as ultracentrifugation, electrophoresis, solubility determination, etc., have been reviewed and criticized on numerous occasions. There is fairly general agreement that no completely satisfactory solution to the problem has yet been developed.

A fundamentally different approach to the estimation of purity was recently described by Williams and Backus.[2] In conjunction with the demonstration of a new technique for determining molecular weight, they used the electron microscope to determine the purity of bushy stunt virus protein preparations. The purity assay consisted of a careful examination of a large number of electron microscope fields for presence or absence of foreign particles.

As the authors pointed out, it is obvious that particles with size below the limit of resolution of the electron microscope go undetected by this method. Furthermore, particles present in small number, even though they be very large, might be overlooked. The authors also discussed this latter limitation; nevertheless, they concluded from the use of the electron microscope that the contamination of their preparations by particles of relatively large size was less than 1%.

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(1) Publication No. 2 of the Department of Biophysics.

(2) R. C. Williams and R. C. Backus, THIS JOURNAL, **71**, 4052, 1949. See also Williams, Backus and Steere THIS JOURNAL **73**, 2062 (1951).