The steam nonvolatile basic residue (750 mg., m.p. 125–132°) was crystallized from acetone–petroleum ether to give pure *p*-aminopropiophenone, m.p. 140–142°.

Yields of 19, 18–20, and 20–23% of aniline, *o*-aminopropiophenone, and *p*-aminopropiophenone, respectively, were obtained in a series of identical experiments.

Irradiation of Butyranilide. Method B.—Butyranilide (3 g.) in anhydrous ethanol (100 ml.) was irradiated for 18 hr. The usual work-up led to a steam-volatile basic fraction (930 mg.) which was shown by g.l.c. to consist of *o*-aminobutyrophenone (510 mg., 17%) and aniline (420 mg., 20%). *o*-Aminobutyrophenone was separated from aniline by vacuum distillation; it was crystallized from petroleum ether (refrigerator) and showed m.p. 46–48° (lit.[17] m.p. 45°).

p-Aminobutyrophenone (700 mg., m.p. 81–87°) was isolated from the steam nonvolatile residue. After crystallization from acetone–petroleum ether it exhibited m.p. 95–97° (lit.[18] m.p. 94–95°). Unreacted butyranilide could be isolated from the reaction mixtures.

Irradiation of Benzanilide. Method A.—Benzanilide (10.00 g.) dissolved in 500 ml. of anhydrous ethanol in the apparatus already described was irradiated for 3 days. After irradiation the alcohol was evaporated on a steam bath. The residue was extracted with ether and the undissolved solid was filtered. This contained 6.75 g. of starting material. The ether solution was extracted twice with 10% HCl and the aqueous part was neutralized with 10% sodium hydroxide and extracted with ether. V.p.c. of this solution indicated a trace of aniline. Evaporation of the ether solution after washing and drying over anhydrous magnesium sulfate gave a solid, which on crystallization twice from benzene–petroleum ether using decolorizing charcoal gave 0.38 g. (12%) of white crystalline needles of *p*-aminobenzophenone, m.p. 123–124° (lit.[19] m.p. 123–124°).

The original ether solution was then extracted with 10% sodium bicarbonate solution. The aqueous portion produced 0.55 g. (27%) of a white solid after acidification followed by extraction with ether. This solid was found to be identical with an authentic sample of benzoic acid.

The residual ether solution was concentrated and chromatographed over neutral alumina. With petroleum ether (b.p. 60–70°) in earlier fractions 0.15 g. (6%) of a liquid is obtained. It had an identical retention time with that of an authentic sample of ethyl benzoate. Further chromatography, using petroleum ether, gave a yellow solid, which upon crystallization followed by vacuum sublimation and a final crystallization gave 0.45 g. (14%) of bright yellow crystals of *o*-aminobenzophenone, m.p. 105–106° (lit.[20] m.p. 105–106°).

Carbon Monoxide and Hydrogen Determination.—Butyranilide (10.5 g.) was dissolved in 700 ml. of dry, distilled ethanol. The solution was degassed by bubbling nitrogen through the solution in the irradiation vessel. The solution was sealed with a space at the top of the containing vessel filled with nitrogen and irradiated with a Hanovia 550-w. lamp for 24 hr. The accumulated gases over the reaction mixture were displaced into a deflated polyethylene bag. This gas was subjected to vapor phase chromatography on a Molecular Sieve 13-A column in a Burrell Kromo-Tog Model K-3 apparatus. Peaks were present on the chromatogram which corresponded to standard samples of CO and H_2. As a further check for CO, the sample gases were passed through a CO-indicating tube (no. 47134)[21] and the color change which occurred indicated the presence of CO.

Acknowledgment.—V. I. S. and D. V. R. wish to express their gratitude to W. Beckering, U. S. Bureau of Mines, Grand Forks, N. D., for the analysis of carbon monoxide and hydrogen and R. E. Engbrecht for conducting the experiments on these analyses.

(17) L. A. Elson, C. S. Gibson, and J. D. A. Johnson, *J. Chem. Soc.*, 1128 (1930).
(18) D. R. Clifford, R. H. Davis, and D. Woodcock, *ibid.*, 5097 (1960).
(19) A. Baeyer and R. Löhr, *Chem. Ber.*, **23**, 1621 (1890).
(20) R. Geigy and W. Koenigs, *ibid.*, **18**, 2400 (1885).
(21) Mine Safety Appliances Co., Pittsburgh, Pa.

Fragmentation of 1,10-Decalindiol Monotosylates[1]

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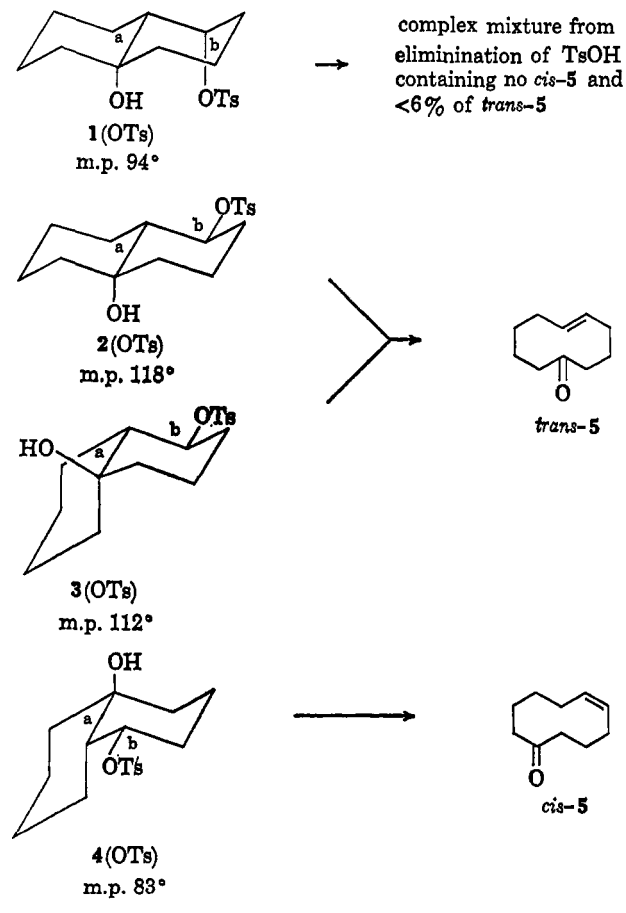
Fragmentations of cyclic 1,3-diol monosulfonates have been shown to be of interest in the syntheses of several cyclononenones[2] and cyclodecenones.[3] We now briefly report additional results in the 1,10-decalindiol → 5-cyclodecenone series which emphasize the synthetic value of the method when antiperiplanar[4] bonds can be broken in the fragmentation.

The four 1,10-decalindiol monotosylates **1**–**4**(OTs) were subjected to the action of potassium *t*-butoxide[5] in *t*-butyl alcohol for 1 hr. at 40°. Monotosylates **2**- and **3**(OTs) were individually converted in high yield

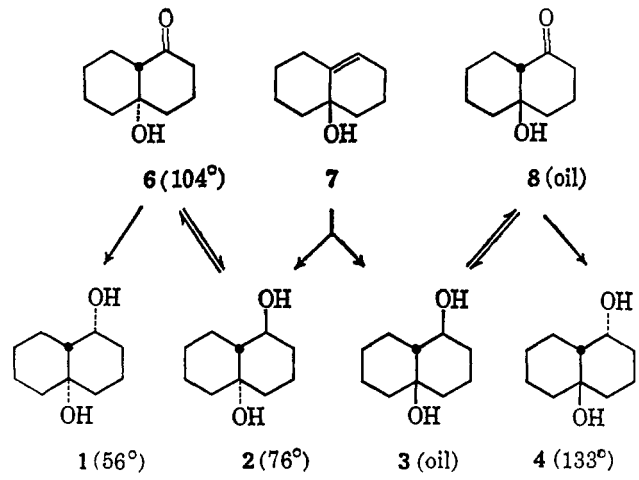


(1) This investigation was supported by Public Health Service Research Grant GM 09759 from the Division of General Medical Sciences, U. S. Public Health Service. Acknowledgment is also made of National Science Foundation Grant G19108 which contributed to the purchase of the n.m.r. spectrometer used in this research.
(2) (a) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964); (b) M. Tanabe and D. F. Crowe, *Tetrahedron Letters*, **No. 40**, 2955 (1964).
(3) (a) P. S. Wharton, *J. Org. Chem.*, **26**, 4781 (1961); (b) P. S. Wharton, G. A. Hiegel, and R. V. Coombs, *ibid.*, **28**, 3217 (1963); (c) H. H. Westen, *Helv. Chim. Acta*, **47**, 575 (1964).
(4) Nomenclature proposed by W. Klyne and V. Prelog [*Experientia*, **16**, 521 (1960)].
(5) R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957).

(>90%) to *trans*-5-cyclodecenone (*trans*-**5**)[6,7] and **4**-(OTs) was converted in similar yield to *cis*-5-cyclodecenone (*cis*-**5**).[7a] These results are in accord with concerted breakage of antiperiplanar (180°) bonds a and b in the conformations of **2**–**4**(OTs) drawn.[8] The stereospecificity of each reaction is evident from the detection by capillary vapor phase chromatography of no more than 0.1% of the unexpected isomer of 5-cyclodecenone in each product.

The importance of geometry is also emphasized by the different behavior on treatment with base of **1**(OTs) in which bonds a and b are necessarily *syn*-clinal[4] (60°). Subjected to the same conditions used to fragment **2**–**4**(OTs), **1**(OTs) yielded a product which contained much unreacted tosylate. Under more drastic conditions, sodium methylsulfinyl carbanion[2a] or prolonged *t*-butoxide treatment, **1**(OTs) disintegrated with loss of tosylate to a mixture of products containing no detectable *cis*-**5**, the product expected from a concerted, albeit difficult, fragmentation. Analyses of the product by infrared spectroscopy and capillary v.p.c. were, however, consistent with the presence of 6% of *trans*-**5** which might be expected from nonconcerted fragmentation *via* a carbonium ion.[8]

Note should be made of the characterization of new compounds involved in this work. Diol monotosylates **2**–**4**(OTs) were prepared by tosylating the corresponding diols in pyridine. Monotosylate **1**(OTs) could not be prepared in pyridine but was obtained by treatment of the diol in ether solution first with sodium hydride and then with tosyl chloride.[9] The 1,10-decalindiols were synthesized by methods which allowed configurational assignments to be made without difficulty. Hydroboration of allylic alcohol **7** gave the previously reported[3b] mixture of two diols which was resolved into its components, one oily, the other crystalline, by *p*-nitrobenzoylation of the diol mixture, fractional crystallization of the *p*-nitrobenzoates, and saponification of the isolated pure *p*-nitrobenzoates. Assignments of configuration **2** to the crystalline diol and **3** to the oily diol were made after examining the infrared spectra of the two diols in dilute carbon tetrachloride solution[3c]: intramolecular hydrogen bonding was apparent only in the spectrum of the oily diol. The two diols were related structurally by oxidation to two different ketols which both yielded the expected ultraviolet spectrum of Δ^9-1-octalone when subjected to mild alcoholic acid or base treatment. Sodium borohydride reduction of the oily ketol **8** obtained from **3** gave a crystalline diol mixture from which a new diol, **4**, m.p. 133°, was obtained in *ca.* 50% yield by simple crystallization. As expected, intramolecular hydrogen bonding was not detected in the infrared spectrum of this diol. Lithium aluminum hydride reduction of the crystalline ketol **6**, m.p. 104°, obtained from **2** gave an oily diol mixture from which another new diol, **1**, m.p. 56° and showing strong intramolecular hydrogen bonding in its infrared spectrum, was obtained by a sequence involving *p*-nitrobenzoylation of the diol mixture, crystallization of a new *p*-nitrobenzoate in *ca.* 50% yield, and saponification of the pure *p*-nitrobenzoate. It is a curious fact that the *p*-nitrobenzoates of **1** and **2** were both found to be dimorphic with identical double melting points, 106 and 113°.



(6) Previously shown for a *mixture* of **2**- and **3**(OTs).[3b]

(7) (a) H. L. Goering, W. D. Closson, and A. C. Olson, *J. Am. Chem. Soc.*, **83**, 3507 (1961); (b) E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *ibid.*, **83**, 2013 (1961).

(8) The recently reported study of fragmentation in the 4-, 5-, and 7-tosyloxy-N-methyldecahydroquinoline series provides an interesting comparison with the reactions reported here. See C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Letters*, **No. 39**, 2901 (1964).

(9) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).

Experimental

Melting points were taken in capillary tubes in a Thomas–Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer; n.m.r. spectra on a Varian A-60 spectrometer. All organic solutions were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure after filtering. Pyridine was dried over barium oxide and distilled, *p*-nitrobenzoyl chloride was crystallized from heptane, and *p*-toluenesulfonyl chloride was used as supplied by Distillation Products Industries.

cis-**Decalin-*cis*-1,10-diol Monotosylate** [**3**(**OTs**)].—A solution of 502 mg. (2.95 mmoles) of diol mixture (obtained from hydroboration of $\Delta^{1(9)}$-10-octalol[3b]) in 5.5 ml. of dry pyridine was treated overnight at 5° with 1.336 g. (7.2 moles) of *p*-nitrobenzoyl chloride. Work-up gave 840 mg. (89%) of a yellow oil, part of which (692 mg.) was dissolved in ether and cooled, yielding a first crop of 203 mg. (26%) of crystals, m.p. 137–141°, which was recrystallized twice from methanol–ether and then sublimed at 0.1 mm. from an oil bath at 115–136° to yield an analytical sample of **3** *p*-nitrobenzoate, m.p. 143–144°.

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.95; H, 6.58; N, 4.39. Found: C, 63.94; H, 6.69; N, 4.39.

Saponification of 2.092 g. (6.56 mmoles) of **3** *p*-nitrobenzoate, m.p. 143–144° (18.5 mmoles of potassium hydroxide in 60 ml. of methanol and 8 ml. of water for 8 hr. at room temperature), yielded, after work-up, 1.075 g. (96%) of a colorless oil which was distilled at 0.1 mm. from an oil bath at 40–60°, $\lambda_{max}^{CCl_4}$ (0.009 *M*) 2.77 and 2.83 μ. Part of the distillate, 884 mg. (5.20 mmoles), was treated overnight at 5° with 1.316 g. (6.90 mmoles) of *p*-toluenesulfonyl chloride in 10 ml. of dry pyridine. Work-up gave 1.622 g. (96%) of white crystals, m.p. 105–108° after softening at 100°, which was recrystallized twice from ether–pentane, yielding 1.23 g. (73%), m.p. 110.5–112°.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.97; H, 7.41; S, 9.88. Found: C, 63.05; H, 7.51; S, 9.83.

trans-**Decalin-*trans*-1,10-diol Monotosylate** [**2**(**OTs**)].—After removal of 203 mg. of almost pure **3** *p*-nitrobenzoate from the *p*-nitrobenzoate mixture as described above, further small crops of crystals were obtained by letting the mother liquor stand. The residue was then dissolved in hot methanol and cooled, giving 231 mg. (29%) of crystals, m.p. 105–110°, which yielded 153 mg., m.p. 112–113°, after crystallization from ether–hexane. Two crystallizations from ether and finally sublimation at 0.1 mm. from an oil bath at 102° gave an analytical sample, m.p. 105–106 and 112–113° after melting and seeding with the higher melting form obtained initially.

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.95; H, 6.58; N, 4.39. Found: C, 64.21; H, 6.78; N, 4.57.

Saponification of 551 mg. of **2** *p*-nitrobenzoate, m.p. 105–106°, yielded, after work-up, 288 mg. (98%) of an oil which crystallized on standing, m.p. 73–75°, $\lambda_{max}^{CCl_4}$ (0.008 *M*) 2.76 μ. Several crystallizations from ether and sublimation at 0.1 mm. from an oil bath at 65° gave an analytical sample, m.p. 75.5–76.5°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.44; H, 10.73.

Tosylation of 862 mg. of **2**, m.p. 69–73°, from saponification of **2** *p*-nitrobenzoate, m.p. 105–106°, yielded 1.600 g. (98%) of white crystals, m.p. 116–117°, which gave 1.12 g. (69%), m.p. 117–118°, after two crystallizations from ether–pentane.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.97; H, 7.41; S, 9.88. Found: C, 62.97; H, 7.60; S, 9.84.

***cis*-Decalin-*trans*-1,10-diol Monotosylate [4(OTs)].**—A solution of 662 mg. (3.89 mmoles) of oily **3** (from saponification of **3** *p*-nitrobenzoate, m.p. 143–144°) in 60 ml. of acetone (previously distilled from potassium permanganate) was stirred for 2 min. at 13° with a solution of 1.02 ml. (1.05 equiv.) of Jones reagent.[10] Work-up gave 603 mg. (92%) of a yellow oil: $\lambda_{max}^{CHCl_3}$ 2.74, 2.80, 2.90, and 5.87 μ. Faint absorption at 6.0 and 6.1 μ showed that little Δ⁹-1-octalone had been formed under the reaction conditions. The oil, 603 mg. (3.58 mmoles), was dissolved in 15 ml. of methanol and stirred for 45 min. at 0° with 304 mg. (8.03 mmoles) of sodium borohydride. Work-up gave 479 mg. (79%) of a colorless, partially crystalline product which gave 263 mg. (43%) of white crystals, m.p. 128.5–131° from ether. Two recrystallizations from methanol–ether–pentane and sublimation at 0.1 mm. from an oil bath at 67–74° gave a sample, m.p. 132–133°, which was submitted for analysis, $\lambda_{max}^{CCl_4}$ (0.006 *M*) 2.79 μ.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C,[11] 70.20; H, 10.77.

p-Nitrobenzoylation of 105 mg. (0.62 mmole) of **4**, m.p. 128.5–131°, gave, after work-up, 195 mg. (99%) of crystals, m.p. 139–141.5°. Two recrystallizations from methanol–ether–pentane and sublimation at 0.1 mm. from an oil bath at 114–124° yielded an analytical sample, m.p. 141.5–142.5°.

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.95; H, 6.58; N, 4.39. Found: C, 63.81; H, 6.62; N, 4.26.

Tosylation of 887 mg. (5.23 mmoles) of **4**, m.p. 132–133°, yielded 1.680 g. (99%) of an oil which gave 1.587 g. (93%) of crystals, m.p. 79–82.5°, when treated with ether–pentane. Further recrystallizations from ether–pentane yielded an analytical sample, m.p. 82–83°.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.97; H, 7.41; S, 9.88. Found: C, 63.02; H, 7.50; S, 9.72.

***trans*-Decalin-*cis*-1,10-diol Monotosylate [1(OTs)].**—A solution of 288 mg. (1.69 mmole) of **2**, m.p. 73–75°, in 35 ml. of acetone was stirred for 2 min. with a solution of 0.66 ml. (1.56 equiv.) of Jones reagent.[10] Work-up gave 281 mg. (99%) of crystals: m.p. 103.5–104°; $\lambda_{max}^{CHCl_3}$ 2.79, 2.87, and 5.88 μ. There was no indication of dehydration to Δ⁹-1-octalone. After three recrystallizations from ether–pentane an analytical sample of **6**, m.p. 103.5–104°, was prepared by sublimation at 0.1 mm. from an oil bath at 60°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 71.43; H, 9.53. Found: C, 71.56; H, 9.68.

A solution of 328 mg. (1.96 mmoles) of **6**, m.p. 103–104°, in 5 ml. of ether was cooled to 0° and treated with 171 mg. (4.51 mmoles) of lithium aluminum hydride. The mixture was allowed to warm to room temperature and stirred for a further 30 min. Work-up gave 331 mg. (99%) of an oil. From another run the 513 mg. (3.02 mmoles) of oil obtained was *p*-nitrobenzoylated, giving, after work-up, 948 mg. (98%) of crystals, m.p. 88–99°. Crystallization from ether–pentane yielded two crops—551 mg., m.p. 102–107°, and 213 mg., m.p. 109.5–111°. Combination of these two crops and recrystallization from ether–pentane gave 571 mg. (56%) of crystals, m.p. 111.5–112.5°. An analytical sample was prepared by short-path distillation at 0.1 mm. from an oil bath at 104–111°, m.p. 104–106°, and m.p. 111.5–112.5° after melting and seeding with the higher melting form obtained initially.

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.95; H, 6.58; N, 4.39. Found: C, 64.00; H, 6.64; N, 4.49.

Saponification of 447 mg. (1.4 mmoles) of **1** *p*-nitrobenzoate, m.p. 111.5–112.5°, gave, after work-up, 238 mg. (100%) of crystals, m.p. 52–54°. Several recrystallizations from ether–pentane yielded an analytical sample, m.p. 54–56°, $\lambda_{max}^{CCl_4}$ (0.002 *M*) 2.78 and 2.85 μ.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.64; H, 10.79.

A mixture of 174 mg. (1.03 mmoles) of **1**, m.p. 53–55°, and 47 mg. (2.0 mmoles) of sodium hydride and 1.6 ml. of ether was warmed in a flask fitted with a condenser and sealed with a septum cap. The mixture was refluxed for 12 hr., ether being injected when necessary to replace vaporized solvent, and then cooled to −10°. A solution of 200 mg. (1.05 mmoles) of *p*-toluenesulfonyl chloride in 2.0 ml. of ether was injected and the reaction mixture was stirred for 1 hr. at *ca.* −10° and then 1 hr. at room temperature. After filtering through a layer of Filter-Cel, brine was added and the mixture was extracted with ether. Further work-up gave 260 mg. (79%) of an oil which crystallized on standing, m.p. 57–83°. Crystallization from ether–pentane yielded 188 mg. (56%), m.p. 92–93.5°, and further crystallizations gave an analytical sample, m.p. 93–94°.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.97; H, 7.41; S, 9.88. Found: C, 63.06; H, 7.37; S, 9.83.

Base Treatment of 2–4(OTs).—General conditions used to fragment **2–4**(OTs) were as follows. Pure tosylate (*ca.* 1 g.) was dissolved in 40 ml. of dry *t*-butyl alcohol, the solution was warmed to 40°, and a solution of *ca.* 3 equiv. of 1 *N* potassium *t*-butoxide in *t*-butyl alcohol added. A white precipitate started to form immediately. After stirring for 1 hr. at 40°, water was added and the solution was extracted with ether. The ether solution was washed with water and the aqueous solution with pentane. The organic solutions were combined and washed with dilute sodium hydroxide solution and then brine. The organic solution was then dried, filtered, and concentrated, finally by evaporation with a slow stream of nitrogen. Most of the residual solvent was removed after a few minutes at 0.1 mm. Analysis of the product was determined by vapor phase chromatography using a 150-ft. Ucon Polar capillary column at 165–170° in conjunction with flame-ionization detection, Disc integrator, and Perkin–Elmer Model 154. The retention times of *cis*- and *trans*-5-cyclodecenone differed by *ca.* 1 min., the *trans* isomer coming off first. There was no overlapping of peaks and 0.1% of one isomer contaminating the other could be detected. The cyclodecenones were identified by comparison of the infrared spectra with those of authentic samples[12] and conversion of *cis*-**5** to its known oxime,[7a] m.p. 110–111°.

3(OTs).—From 1.142 g. (3.46 mmoles) of tosylate was obtained 524 mg. (104%) of a pale yellow oil showing only two peaks on v.p.c. corresponding to solvent and *trans*-**5** (19.0 min.). Short-path distillation at 0.1 mm. from an oil bath at 28–48° yielded 469 mg. (93%) of colorless pure *trans*-**5**, $n^{25}D$ 1.4928. Note that a value $n^{24}D$ 1.4982 is given for material of 98–99% purity.[7b]

2(OTs).—From 1.049 g. (3.24 mmoles) of tosylate was obtained 599 mg. (124%) of a yellow oil showing on v.p.c. besides solvent (18%) only peaks corresponding to *trans*- and *cis*-**5** with relative areas of 99.9:0.1 at 16.0 and 16.8 min., respectively.

4(OTs).—From 833 mg. (2.57 mmoles) of tosylate was obtained 397 mg. (102%) of a yellow oil showing on v.p.c. besides solvent (9%) only *cis*-**5** at 17.0 min. Short-path distillation at 0.1 mm. from an oil bath at 43–51° gave 273 mg. (90%) of colorless pure *cis*-**5**, $n^{25}D$ 1.4967. A value $n^{25}D$ 1.4943–1.4947 is given[7a] for material shown to be pure by packed-column v.p.c.

Base Treatment of 1(OTs). A.—Subjected to the conditions used to fragment **2–4**(OTs), 46 mg. of **1**(OTs) yielded 32 mg. of product still containing organic tosylate. A portion of the product, 28 mg., in 2 ml. of *t*-butyl alcohol was treated further with 0.45 ml. of 1 *N* potassium *t*-butoxide for 19 hr. at 40°. Work-up gave 22 mg. (117%) of an oil still containing a small amount of tosylate: $\lambda_{max}^{CCl_4}$ 2.8–2.9 (w), 5.86–5.88 (broad and weak), 7.3, and 8.5 μ (w); n.m.r. chemical shifts at τ 4.4–4.7 (1H) and 7.5–9.3 (24H). There was no appreciable substitution by *t*-butoxide indicated by the n.m.r. spectrum. Thin layer chromatography on silica gel (ethyl acetate–ethanol 95:5 v./v.) showed six main spots at R_f 0.11, 0.15, 0.20 (all large), 0.27, 0.34, and 0.60 (all small). Capillary v.p.c. at 162° showed six main peaks at 8.0, 8.3 (35% combined), 9.7 (16%), 14.4

(10) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(11) Carbon analysis outside normally acceptable ±0.3% limits.

(12) W. D. Closson, Ph.D. Thesis, University of Wisconsin, 1960.

(37%), 18.1 (6% corresponding to the retention time of authentic *trans*-5), and 24.0 min. (5%).

B.—To 0.2 ml. (1.3 equiv.) of sodium methylsulfinyl carbanion in dimethyl sulfoxide[13] was added 21 mg. of 1(OTs). After 1 hr. at room temperature the mixture was worked up, giving 10 mg. (106%) of a colorless oil: $\lambda_{max}^{CCl_4}$ 2.8 (w), 5.77 (vw), 5.85 (w), 7.3, and 8.5 μ (w). Thin layer chromatography on silica gel (chloroform) showed one large spot at R_f 0.20 (same as $\Delta^{1(9)}$-10-octalol) and small spots at R_f 0.15, 0.26, 0.34, and 0.74.

(13) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

The Conformational Free-Energy Difference of the Nitro Group

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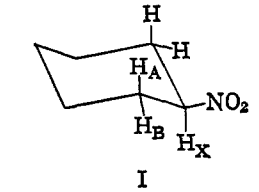
In a recent communication[2] Feltkamp and Franklin have reported an approximate value of 1 kcal./mole for the conformational free-energy difference of the nitro group and that nitrocyclohexane therefore exists approximately 85% in conformer I at 26°. A previous report[3] had suggested that at 26° in 10% w./v. solution in carbon tetrachloride, nitrocyclohexane exists exclusively in conformer I. Feltkamp and Franklin have calculated their values by their published method[4] (a method similar to that reported by Garbisch[5] for measuring the equilibrium constants of mobile six-membered ring systems) from the band widths of the n.m.r. multiplets of the X proton of nitrocyclohexane and of *trans*-4-*t*-butylnitrocyclohexane obtained from the literature, and approximated for *cis*-4-*t*-butylnitrocyclohexane. No mention is made of solvent.[6]



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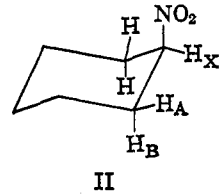
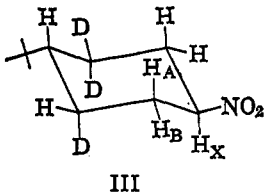
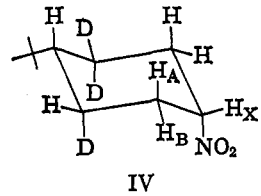


II



III



IV

In continuing our n.m.r. study of nitrocyclohexanes[7-9] we have now measured the conformational preference of the nitro group in nitrocyclohexane neat, in 33 and 50 mole % in deuterated chloroform, and in 20 and 33 mole % in acetone and in acetonitrile at 37° by the signal-width method,[4,5] using the partially deuterated compounds *trans*- and *cis*-4-*t*-butylnitrocyclohexane-3-(axial),5,5-d_3 (III and IV, respectively) for conformationally homogeneous models. The deuterated compounds give simplified spectra which afford more accurate measurements of coupling constants and signal band widths. No appreciable difference was found in the conformational preference of nitrocyclohexane in the pure state and in the two dilutions in deuterated chloroform at 37°. Under these conditions a value of 78 ± 4% of conformer I (K = 3.5 ± 0.5) was found, and a conformational free-energy difference (ΔG) of 0.78 ± 0.10 kcal./mole was obtained for the nitro group. No appreciable difference was found in acetone and acetonitrile or between the two concentrations used in each solvent. In these solvents 79.5% of conformer I was obtained by using the signal band width of III and IV measured in deuterated chloroform as reference. The measurements were made from average band-width values obtained from at least four spectra in each dilution in each solvent. The reproducibility of measurements of band widths was about ±0.2 c.p.s.

Using the notation of Garbisch[5] the band width of the X proton equals $2J_I = 2(J_{AX} + J_{BX})$ in III; $2J_{II} = 2(J_{AX} + J_{BX})$ in IV; and $2J^\circ = 2(N_I J_{aa} + N_{II} J_{ee} + N_I J_{ea} + N_{II} J_{ae})$ in the mobile nitrocyclohexane, where N_I and N_{II} are mole fractions of conformers I and II, respectively.

$$N_I = \frac{J^\circ - J_{II}}{J_I - J_{II}} \qquad K = \frac{J^\circ - J_{II}}{J_I - J^\circ}$$

The spectra were determined at 60 Mc. at 37° with a Varian A-60 spectrometer. The spectrum of III in deuterated chloroform gave ν_X = 259 c.p.s., $2J_I$ = 31.6 c.p.s., J_{aa} = 11.6, and J_{ea} = 4.2 c.p.s. Our reported values for J_{aa} and J_{ae} obtained from the nondeuterated compound[7] were 11.3 and 4.2 c.p.s. The spectrum of IV gave ν_X = 270.5 c.p.s. and $2J_{II}$ = 13.5 c.p.s. Accurate values of J_{ae} and J_{ee} could not be obtained from the spectrum of IV, but they are not equal. The spectrum of nitrocyclohexane neat, as well as in the two dilutions in deuterated chloroform, gave ν_X = 263 c.p.s. and a signal band width $2J^\circ$ = 27.6 c.p.s. The chemical shifts of the X protons are too close for reliable calculation of ΔG by the chemical shift method of Eliel.[10]

The deuterated compounds II and IV were obtained from the trideuterated 4-*t*-butylcyclohexanone-3(axial),-5,5-d_3 by the method reported for the corresponding nondeuterated compounds.[7] The trideuterated ketone was obtained by iodine-catalyzed dehydration of a mixture of *cis* and *trans* isomers of 4-*t*-butyl-4-hydroxycyclohexanol-3,3,5,5-d_4[11] followed by platinum-catalyzed hydrogenation of the trideuterated alkene and subsequent chromic acid oxidation of the secondary alcohol by the method of Brown and Garg.[12]

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