[Contribution from the Wm. H. Nichols Chemical Laboratory, New York University]

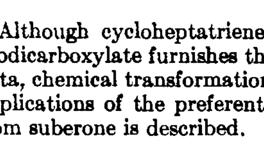
The Reaction of Cycloheptatriene with Ethyl Azodicarboxylate

J. MARSHALL CINNAMON and KARL WEISS[1]

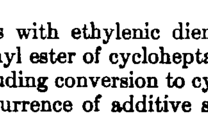
Received October 24, 1960

Although cycloheptatriene reacts with ethylenic dienophiles to produce Diels-Alder adducts, its reaction with ethyl azodicarboxylate furnishes the diethyl ester of cycloheptatrienylbicarbamic acid. This structure was established by spectral data, chemical transformations including conversion to cycloheptylhydrazine, and an alternative synthesis. The mechanistic implications of the preferential occurrence of additive substitution are discussed. The synthesis of cycloheptylhydrazine from suberone is described.

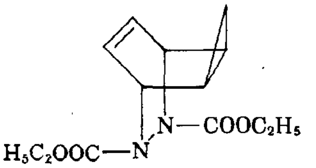
The reactions of azodicarboxylic esters with hydrocarbons follow two main paths. Additive substitution occurs with olefins bearing allylic hydrogen, and with aromatic hydrocarbons.[2-5] With the latter, depending on the conditions, either nuclear or side-chain substituted products are obtained. On the other hand, the azodicarboxylic esters behave as reactive dienophiles toward conjugated dienes[6] and anthracene[7]; with styrenes, both modes of reaction take place.[8] Thus cyclopentadiene and ethyl azodicarboxylate produce I in a reaction which is entirely analogous to the interaction of this diene with maleic anhydride.[9] Since cycloheptatriene and its substitution products undergo the Diels-Alder reaction with a variety of ethylenic dienophiles to form adducts which are formally derived from norcaradiene (*cf.* II),[10] a parallel reaction with azo ester should produce the adduct III.



I



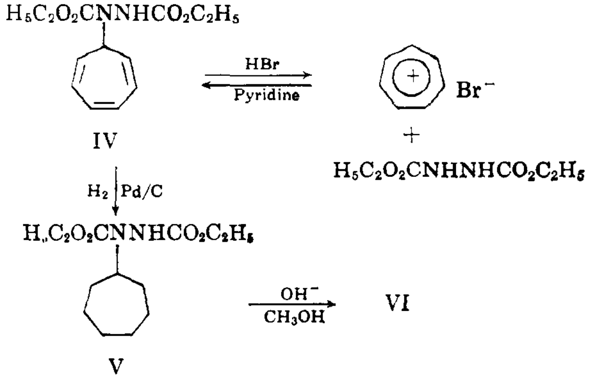
II



III

The azo ester and cycloheptatriene were found to react rapidly and exothermically at room temperature, either with or without solvent. However, the product was not adduct III. Instead, the additive substitution of a methylenic hydrogen atom resulted in the quantitative formation of diethyl cycloheptatrienylbicarbamate (IV), the structure of which was proven as follows. The infrared spectrum shows a strong band at 3300 cm.$^{-1}$ (N—H), as well as bands which are characteristic of the cycloheptatriene system in the 700–760 cm.$^{-1}$ region.[11] The ultraviolet spectrum in ethanol (λ_{max} 257 mμ, log ϵ 3.50; λ_{min} 224 mμ, log ϵ 3.04) is quite typical for a 7-substituted cycloheptatriene.[11,12]

The passage of anhydrous hydrogen bromide into an ethereal solution of IV produced an almost quantitative precipitate of tropylium bromide, which was identified by its properties and infrared spectrum.[12a] Ethyl hydrazodicarboxylate was isolated from the filtrate. The catalytic hydrogenation of IV (3.15 molar equivalents of hydrogen absorbed) resulted in the formation of diethyl cyclo-



---

[1] To whom enquiries should be sent. Present address: Department of Chemistry, Northeastern University, Boston 15, Mass.

[2] K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943).

[3] R. Huisgen, F. Jakob, W. Siegel, and A. Cadus, *Ann.*, **590**, 1 (1954).

[4] R. Huisgen and F. Jakob, *Ann.*, **590**, 37 (1954).

[5] R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960).

[6] O. Diels, J. H. Blom, and W. Koll, *Ann.*, **443**, 242 (1925); P. Baranger and J. Levisalles, *Bull. soc. chim. France*, 704 (1957).

[7] O. Diels, S. Schmidt, and W. Witte, *Ber.*, **71**, 1186 (1938); K. Alder and H. Niklas, *Ann.*, **585**, 81 (1954).

[8] K. Alder and H. Niklas, *Ann.*, **585**, 97 (1954); N. Rabjohn and H. M. Molotsky, *J. Am. Chem. Soc.*, **77**, 2907 (1955).

[9] Because of the unknown isomeric composition of the azo ester, the disposition of the carbethoxy groups in I and III is arbitrary. Attempts to separate alkyl azodicarboxylates into their geometrical isomers have been unsuccessful. See ref. 22.

[10] See K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953), K. Alder, R. Muders, W. Krane, and P. Wirtz, *Ann.*, **627**, 59 (1960), and earlier references cited therein.

[11] K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

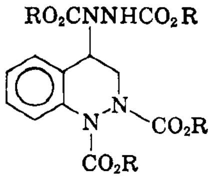
[12] (a) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954); (b) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

heptylbicarbamate (V). The hydrolysis of V with sodium hydroxide in aqueous methanol afforded cycloheptylhydrazine (VI), which was isolated as its oxalate in 37% yield. The structure of VI was proved by independent synthesis.

Compound IV was also obtained from the reaction of tropylium bromide with ethyl hydrazodicarboxylate in the presence of pyridine. The identity of the product of this reaction with that from the azo ester was established *via* infrared spectra.

Cycloheptylhydrazine was prepared from suberone by two methods. The catalytic hydrogenation of cycloheptylidenehydrazine was not successful. Although with Adams' catalyst slightly more than the theoretical amount of hydrogen was absorbed in one week, only unchanged hydrazone and dicycloheptylidenehydrazine (68% yield) could be isolated. Cycloheptylhydrazine was, however, obtained in 8% yield from the reduction of the hydrazone with an excess of sodium in ethanol. A more efficient method of preparation consisted of the conversion of suberone to ethyl 3-cycloheptylidenecarbazate, which was smoothly hydrogenated over platinum-on-carbon to ethyl 3-cycloheptylcarbazate. The basic hydrolysis of the latter ester, which proceeded *via* the isolable sodium salt of cycloheptylcarbazic acid, afforded VI in 59% yield.[13] Cycloheptylhydrazine is a colorless liquid which rapidly deteriorates in air. Its stable oxalate and dibenzoyl derivative served to identify the product of the hydrolysis of V.

It is evident that, in the azo ester–cycloheptatriene system, additive substitution represents an energetically more favorable path than the normal diene reaction. The only other examples of preference for this process in systems where a diene reaction is formally possible appear to be the formation of compounds of structure VII from styrenes,[8] and of an analogously constituted product from styrene and maleic anhydride.[14] These compounds may be viewed as arising from a diene reaction followed by a re-aromatizing additive substitution.

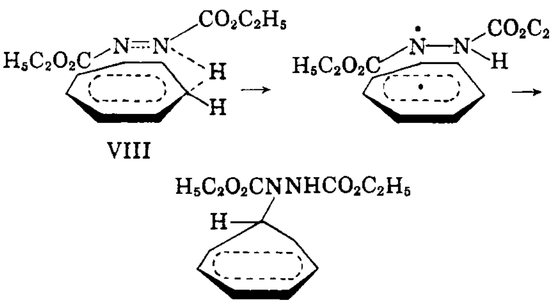


VII

Evidence has been presented for the operation of two distinct mechanisms in the additive substitution reactions of azo esters with other olefins. Catalysis by benzoyl peroxide and other radical initiators, as well as inhibition by typical chain inhibitors, support a chain mechanism involving allyl-type radicals for the interaction of azoester with cyclohexene.[4,5] By contrast, the reaction of azoester with 1,3-diarylpropenes, and with 1,2- and 1,4-dihydronaphthalene is not affected by radical initiators and inhibitors, and proceeds with an obligatory shift of the double bond. The concerted addition-abstraction mechanism proposed for these reactions is supported by a lack of a pronounced solvent effect on the rate.[5]

In the reaction of cycloheptatriene with azo ester one can envision that the actual or incipient formation of the stabilized cycloheptatrienyl radical,[15] as well as the retention of the *pseudo*-aromatic cycloheptatriene structure[16] in the product, provide the driving force for additive substitution. As, in general, stabilized radicals function only poorly as chain carriers[17] a mechanism, proceeding *via* transition state VIII, in which hydrogen abstraction[18] is followed by the almost simultaneous formation of the carbon-nitrogen bond, appears to be reasonable.[19]

An alternative mechanism[20] is suggested by the ready reaction of cycloheptatrienes with trityl salts to produce the corresponding tropylium ions.[21] Thus it is conceivable that hydride ion abstraction



---

[13] The preparation of alkylhydrazines by this sequence of reactions is described by J. R. Geigy, A.G., Swiss Pat. 307,629 (1955).

[14] K. Alder and R. Schmitz-Josten, *Ann.*, **595**, 1 (1955).

(15) J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952); W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

(16) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956); M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1960).

(17) *Cf.* C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, pp. 162–164, 263–265.

(18) The ability of azo esters to accept hydrogen has already been noted; see ref. 3, p. 3. Also, the dicarbethoxyhydrazyl radical appears to be relatively stable; see G. O. Schenck and H. Formanek, *Angew. Chem.*, **70**, 505 (1958).

(19) Steric relationships in VIII (examined with models developed by G. Brumlik, Abstracts, 137th Natl. Am. Chem. Soc. Meeting, Cleveland, Ohio, April, 1960, p. 8-F) indicate that if the new bond formation occurs so rapidly that the nuclei remain essentially stationary, the substituent would probably be introduced in the 2-position of cycloheptatriene. In any case, the proposed mechanism should be distinguishable from others involving a different orientation of the reactants by the use of appropriately labelled cycloheptatriene; *cf.* ref. 5, p. 534.

(20) Kindly pointed out by the referee.

(21) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); H. J. Dauben, Jr., and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

furnishes an ion-pair (tropylium ion and hydrazine anion) which collapses to IV. The evidence at hand does not allow a distinction to be made between the two paths.

The qualitative observation, that the rate of the cycloheptatriene–azo ester reaction is not significantly influenced by benzoyl peroxide or benzoquinone, does not unequivocally rule out a radical chain mechanism. The temperature was quite low (30°) for the appreciable generation of radicals by the peroxide. Also, the possible participation of the quinone in a diene reaction must be considered. In the presence of acids, the reaction appeared to take a different course as evidenced by discoloration and tar formation.

EXPERIMENTAL[22]

Cycloheptatriene. The hydrocarbon was distilled before use (b.p. 115° (760 mm.)), and stored at −20° under nitrogen. Quantitative hydrogenation showed the cycloheptatriene content to be a minimum of 87%, the remainder being mainly toluene.

Ethyl azodicarboxylate. This compound was prepared according to the method of Rabjohn.[23] The physical constants agreed with those reported.[24]

Diethyl cycloheptatrienylbicarbamate (IV). (a) *From cycloheptatriene and ethyl azodicarboxylate.* Ethyl azodicarboxylate (3.48 g., 0.02 mole) and cycloheptatriene (2.12 g., 0.02 mole) were mixed without solvent at 0°. The mixture was then allowed to warm slowly to room temperature. After standing overnight, the originally mobile, orange-colored liquid became very viscous and the color faded to a very pale yellow. According to its infrared spectrum the product, at this point, was already essentially pure IV. Molecular distillation at 75° and 1×10^{-5} mm. pressure furnished pure IV as an almost colorless viscous liquid, which was converted into a colorless solid, m.p. 69–71° by trituration with pentane at −80°. Alternatively, the crude product may be solidified directly, but its recrystallization is rendered difficult by the tendency to reappear as an oil from solution. The compound deteriorated only very slowly on prolonged storage in air. Infrared spectrum (potassium bromide): bands at 3300 cm.$^{-1}$ (N—H), at 1705 and 1720 cm.$^{-1}$ (C═O),[25] and at 742 and 708 cm.$^{-1}$ (cycloheptatriene system).

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.6; 6.8; N, 10.5. Found: C, 58.7; H, 6.9; N, 10.5.

For subsequent reactions with IV, it was found convenient to use the liquid, undistilled product after the removal of traces of starting materials under reduced pressure.

To ascertain the effect of benzoyl peroxide and benzoquinone, three mixtures of 0.01 mole of each cycloheptatriene and azo ester, one containing 100 mg. of the peroxide and another containing 100 mg. of quinone, were kept at 30° for 12 hr. Periodic examination of viscosity and color showed that there were no marked differences in the reaction rates of the three samples.

(b) *From tropylium bromide and ethyl hydrazodicarboxylate.* To a solution of ethyl hydrazodicarboxylate[23] (0.175 g., 1.0 mmole) in a mixture of 1 ml. of pyridine and 1 ml. of tetrahydrofuran was added 0.343 g. (2.0 mmoles) of tropylium bromide (prepared by the method of Doering and Knox).[12b] The mixture was warmed with stirring on the steam bath for a few minutes, cooled, and diluted with 10 ml. of water. Extraction with ether, washing the ethereal solution with water until neutral, and evaporation of the dried solution gave 0.276 g. of a viscous, orange-colored oil. This oil was extracted with 30 ml. of boiling pentane in 3-ml. portions to separate a small quantity of insoluble, unchanged hydrazo ester. Concentration of the pentane solution and cooling furnished a colorless solid which, after recrystallization from pentane, amounted to 30 mg. and had m.p. and mixture m.p. (with IV from azo ester) 69–71°.

The infrared spectra of this material and IV prepared above were identical.

Reaction of IV *with hydrogen bromide.* Compound IV (5.32 g., 0.02 mole of unpurified product of the azo ester reaction) was dissolved in 200 ml. of absolute ether. Anhydrous hydrogen bromide was passed into the solution until the precipitation appeared to be complete. Filtration, washing with ether, and vacuum drying gave 3.50 g. (100%) of crude tropylium bromide, m.p. 167° dec. The salt, after two crystallizations from nitromethane-ether, had m.p. 207° dec. (lit.[12b] 203° dec.), and an infrared spectrum identical with that of authentic material.[12a]

Anal. Calcd. for C_7H_7Br: C, 49.2; H, 4.1; Br, 46.7. Found: C, 49.3; H, 4.4; Br, 46.7.

Evaporation of the filtrate left 3.39 g. (96%) of impure ethyl hydrazodicarboxylate. Recrystallization from ethanol gave the pure compound, m.p. and mixture m.p. 133–134°.

Hydrogenation of IV. Compound IV (13.3 g., 0.05 mole of unpurified product of the azo ester reaction) was dissolved in 100 ml. of ethyl acetate, 1.0 g. of 5% palladium-on-charcoal was added, and the mixture was hydrogenated with external cooling in a Paar low pressure hydrogenation apparatus. In 75 min. 3.15 molar equivalents of hydrogen were absorbed. The filtered solution was evaporated, and the residual liquid was distilled under vacuum. After a forerun containing a little solid ethyl hydrazodicarboxylate (hydrogenolysis product), *diethyl cycloheptylbicarbamate* (V), b.p. 125° (2×10^{-3} mm.) and n_D^{24} 1.4730, was collected in 47% yield as a colorless, viscous liquid. The compound could not be crystallized. Infrared spectrum: bands at 3390 and 3280 cm.$^{-1}$ (free and bonded N—H), and at 1700 and 1750 cm.$^{-1}$ (C═O)[25] (in chloroform); no bands in the 760–680 cm.$^{-1}$ region (neat liquid).

Anal. Calcd. for $C_{13}H_{24}N_2O_4$: C, 57.3; H, 8.9; N, 10.3. Found: C, 57.3; H, 8.7; N, 10.45.

Hydrolysis of V. In a flask fitted with a magnetic stirrer and a reflux condenser, a mixture of 2.09 g. (7.7 mmoles) of V, 3.70 g. (46.2 mmoles) of 50% by weight aqueous sodium hydroxide solution, and 3 ml. of methanol was heated under nitrogen at 100° for 1 hr. A colorless solid precipitated during the reaction. With efficient cooling, the mixture was first carefully acidified with concentrated hydrochloric acid (gas was evolved), then made basic again with sodium hydroxide, and was finally extracted with 100 ml. of ether in 10-ml. portions. Concentration of the dried ether solution to 10 ml. and the addition of a solution of 1.4 g. of anhydrous oxalic acid in 10 ml. of absolute alcohol precipitated 0.534 g. of the oxalate of VI, m.p. 203° dec. The filtrate furnished another 0.078 g. of material, m.p. 199° dec., bringing the yield to 0.612 g. (37%). The colorless solid had m.p. 204°

---

(22) All melting points are corrected, and boiling points uncorrected. Microanalyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The infrared spectra were determined with a Baird model 4-55 recording spectrometer, and the ultraviolet spectrum with a Beckman DK-2 spectrophotometer.

(23) N. Rabjohn, *Org. Syntheses*, Coll. Vol. III, 375 (1955).

(24) A. Rodgman and G. F. Wright, *J. Org. Chem.*, 18, 465 (1953).

(25) It will be noted that both V and IV show multiplicity in the carbonyl region. This was also found to be the case with ethyl hydrazodicarboxylate, which has bands at 1690 and 1745 cm.$^{-1}$ Yet ethyl azodicarboxylate shows a single band at 1770 cm.$^{-1}$

dec. after two recrystallizations from absolute ethanol. The infrared spectra of this salt and of the oxalate of authentic VI were identical.

Anal. Calcd. for $C_9H_{18}N_2O_4$: C, 49.5; H, 8.3; N, 12.8. Found: C, 49.8; H, 8.5; N, 12.9.

In another hydrolysis experiment using methanolic potassium hydroxide, cycloheptylhydrazine oxalate was obtained in 26% yield. By extraction of the acidified reaction mixture with methylene chloride a viscous liquid of b.p. 92–100° (0.05 mm.) was obtained which, by analysis, appeared to be a mixture of partially decarboxylated and transesterified products.

The dibenzoyl derivative of VI was prepared by refluxing a mixture of 0.55 g. (2.5 mmoles) of the oxalate, 0.73 g. (5.2 mmoles) of benzoyl chloride, and 0.71 g. (6.7 mmoles) of anhydrous sodium carbonate, and 15 ml. of benzene for 2 hr. The colorless compound crystallized from the hot benzene filtrate (0.40 g., m.p. 178–182°). After two recrystallizations from absolute ethanol the m.p. was 207–208°; it was not raised by further recrystallization. This derivative also had an infrared spectrum identical with that of an authentic sample.

Anal. Calcd. for $C_{21}H_{24}N_2O_2$: C, 75.0; H, 7.2; N, 8.3. Found: C, 75.5; H, 6.8; N, 8.5.

Ethyl 3-cycloheptylidenecarbazate. Ethyl carbazate[26] (10.5 g., 0.1 mole) and suberone (11.5 g., 0.1 mole) were dissolved in 25 ml. of benzene. When the initial exothermic reaction was over, the solution was refluxed briefly, and then the water formed was removed by distillation of the benzene as fresh benzene was slowly added. Evaporation to dryness left 20.0 g. (100%) of colorless crystals, m.p. 77–78°. The purified compound (16.9 g., m.p. 79–80°) was obtained by recrystallization from ligroin. Infrared spectrum (potassium bromide): bands at 3260 cm.$^{-1}$ (N—H), and at 1705 cm.$^{-1}$ (shoulder) and 1685 cm.$^{-1}$ (C═N, C═O).

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.6; H, 9.15; N, 14.1. Found: C, 60.9; H, 9.4; N, 13.9.

Ethyl 3-cycloheptylcarbazate. Ethyl 3-cycloheptylidenecarbazate (50.0 g., 0.252 mole) in 150 ml. of absolute ethanol was hydrogenated in the presence of 2.5 g. of 5% platinum-on-carbon in a Paar low pressure hydrogenation apparatus. The theoretical amount of hydrogen was absorbed in 6 hrs. Filtration, evaporation of the solvent, and distillation under vacuum gave 46.1 g. (91%) of a colorless viscous liquid, b.p. 87–90° (0.05 mm.) and n_D^{26} 1.4800, which solidified on standing to colorless crystals, m.p. 40–41° after recrystallization from pentane. Infrared spectrum (neat liquid): bands at 3340 cm.$^{-1}$ (N—H) and 1710 cm.$^{-1}$ (C═O).

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 60.0; H, 10.1; N, 14.0. Found: C, 60.2; H, 10.3; N, 14.1.

Cycloheptylhydrazine (VI). A stirred mixture of 30.0 g. (0.15 mole) of ethyl cycloheptylcarbazate, 36.0 g. (0.45 mole) of 50% by weight sodium hydroxide solution, and 30 ml. of methanol was refluxed under nitrogen (oil bath at 100°) for 2 hr. A voluminous crystalline precipitate appeared, which did not dissolve when the cooled reaction mixture was diluted with 100 ml. of water. A small portion of this material was filtered, and was identified as the monohydrated *sodium salt of 3-cycloheptylcarbazic acid.* The salt evolved carbon dioxide when treated with acid, and the addition of base to the acidic solution liberated the hydrazine.

Anal. Calcd. for $C_8H_{17}N_2O_3Na$: C, 45.3; H, 8.1; N, 13.2. Found: C, 45.6; H, 8.1; N, 13.2.

The suspension was therefore cautiously acidified with concentrated hydrochloric acid, and then made basic with sodium hydroxide. Exhaustive extraction with ether, followed by evaporation of the dried solution and distillation under vacuum gave 11.3 g. (59%) of VI, b.p. 88° (5.5 mm.) and n_D^{26} 1.4922–1.4902 (changes during measurement). Infrared spectrum (neat liquid): bands at 3280 cm.$^{-1}$ (N—H) and 1603 cm.$^{-1}$ (NH_2). Cycloheptylhydrazine is a colorless, mobile liquid with an amine-like odor, which decomposes rapidly in air, but is stable when stored under nitrogen at −20°.

Anal. Calcd. for $C_7H_{16}N_2$: C, 65.6; H, 12.6; N, 21.85. Found: C, 65.6; H, 12.8; N, 21.75.

When the hydrolysis of the ester was carried out with aqueous sodium hydroxide in the absence of methanol[27] the yield of VI was only 27%, and a large amount of starting material was recovered.

The oxalate of VI (m.p. 195–198° dec.) was obtained in quantitiative yield from an ethereal solution of the hydrazine and oxalic acid in ethanol. Two recrystallizations from absolute ethanol raised the m.p. to 201° dec. Infrared spectrum (potassium bromide): bands at 3350 and 3280 cm.$^{-1}$ (N—H), 3050 and 1630 cm.$^{-1}$ (NH_3^+), and at 1703 and 1595 cm.$^{-1}$ (C═O, COO^-).

Anal. Calcd. for $C_9H_{18}N_2O_4$: C, 49.5; H, 8.3; N, 12.8. Found: C, 49.6; H, 8.3; N, 13.0.

The dibenzoyl derivative of VI was prepared from the oxalate as described previously. The compound had m.p. 213.5–214.5° after two recrystallizations from absolute ethanol. Infrared spectrum (potassium bromide): bands at 3430 and 3240 cm.$^{-1}$ (N—H), and at 1675 and 1630 cm.$^{-1}$ (C═O).

Anal. Calcd. for $C_{21}H_{24}N_2O_2$: C, 75.0; H, 7.2; N, 8.3. Found: C, 75.6; H, 7.4; N, 8.4.

Cycloheptylidenehydrazine. This compound was prepared from suberone and hydrazine hydrate as described in the literature.[28] The colorless, mobile liquid had b.p. 84–86° (1.5 mm.) and n_D^{23} 1.5151 (reported[28] b.p. 109–110° (11 mm.) and n_D^{19} 1.5132). Infrared spectrum (neat liquid): bands at 3360 and 3200 cm.$^{-1}$ (N—H), 1625 cm.$^{-1}$ (C═N), and 1603 cm.$^{-1}$ (NH_2).

Anal. Calcd. for $C_7H_{14}N_2$: C, 66.6; H, 11.2; N, 22.2. Found: C, 66.9; H, 11.4; N, 22.2.

Catalytic hydrogenation of cycloheptylidenehydrazine. In a Paar low pressure hydrogenation apparatus, a solution of 25.2 g. (0.2 mole) of suberone hydrazone in 75 ml. of absolute alcohol was hydrogenated over 0.25 g. of Adams' catalyst. In 1 week 1.06 molar equivalents of hydrogen were absorbed. Evaporation of the filtered solution and distillation under vacuum gave 8.0 g. of unchanged hydrazone and 15.0 g. (68%) of crude dicycloheptylidenehydrazine, b.p. 117–126° (1.0 mm.). The pure azine was obtained as an almost colorless liquid, b.p. 112–113° (0.06 mm.) and n_D^{26} 1.5209, by redistillation. Infrared spectrum (neat liquid): band at 1625 cm.$^{-1}$ (C═N).

Anal. Calcd. for $C_{14}H_{24}N_2$: C, 76.3; H, 11.0; N, 12.7. Found: C, 76.1; H, 11.1; N, 12.5.

Authentic dicycloheptylidenehydrazine, prepared according to Overberger *et al.*, [29] had b.p. 109–110° (0.09 mm.), n_D^{26} 1.5218 (reported[29] b.p. 114° (0.3 mm.) and n_D^{21} 1.5210), and an infrared spectrum identical with that of the above material.

Reduction of cycloheptylidenehydrazine with sodium in ethanol. Sodium (31.2 g., 1.35 g.-atoms) was added over a period of 2 hr. to a solution of 30.0 g. (0.24 mole) of the hydrazone in 400 ml. of absolute ethanol. When all reaction had ceased, the alcohol was distilled and the residual liquid

---

(26) Prepared by the method of O. Diels, *Ber.*, **47**, 2183 (1914).

(27) *Cf.* ref. 13.

(28) M. B. Turova-Pollak and F. P. Sidel'kovskaya, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 817 (1941); *Chem. Abstr.*, **36**, 4099^4 (1942).

(29) C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

was distilled under vacuum. After 1.1 g. of an unidentified forerun (b.p. 31–84° (5.0 mm.)), 2.5 g. (8%) of VI was collected as a colorless liquid, b.p. 87–88° (5.0 mm.). The identity of this material was established by its infrared spectrum, and by the spectrum of its oxalate, m.p. 207° dec.

Acknowledgment. We are grateful to the Shell Chemical Corporation for a generous supply of cycloheptatriene.

NEW YORK 53, N.Y.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF WASHINGTON]

Proton Magnetic Resonance Spectra and Stereochemistry of 2-*o*-Tolylcyclohexanol[1]

ALAIN C. HUITRIC AND JOHN B. CARR

Received December 1, 1960

The reduction of 2-*o*-tolylcyclohexanone has been investigated by three methods and the reduction mixture analyzed by gas chromatography. Cyclopentylmagnesium bromide gave a mixture of *cis*- and *trans*-2-*o*-tolylcyclohexanol in the ratio of 60% *cis* and 40% *trans*; diphenyltin dihydride yielded 85% *trans* and 15% *cis* and isobutylmagnesium bromide gave an overall yield of about 50% *cis* plus some unidentified material and traces of *trans*. Pure *cis* was obtained through separation of the α-naphthylurethans with subsequent reduction with lithium aluminum hydride–aluminum chloride mixture. The NMR spectra of *cis*- and *trans*-2-*o*-tolylcyclohexanol and their acetates are consistent with structures in which the cyclohexane ring is in a chair conformation with the tolyl group in equatorial orientation. The spectra confirm that the spin-spin coupling constant between neighboring hydrogens in axial orientation is much larger than between neighboring hydrogens in other orientations.

The reduction of substituted cyclohexanones affords synthetic routes to the corresponding *cis* and *trans* cyclohexanols, but as was demonstrated by Hardy and Wicker[2] the stereochemistry of many reduction methods is still unpredictable and the assignment of configuration to the resulting substituted cyclohexanols solely on generalyzed rules is still hazardous. In the present work three methods of reduction of 2-*o*-tolylcyclohexanone were investigated for stereospecificity: diphenyltin dihydride,[3] isobutylmagnesium bromide, and cyclopentylmagnesium bromide. The products were analyzed for percentage *trans*-2-*o*-tolylcyclohexanol (I) and *cis*-2-*o*-tolylcyclohexanol (II) by analytical gas chromatography. Pure I was prepared by the stereospecific reaction of *o*-methylphenyllithium and cyclohexene oxide. The proton magnetic resonance spectra of I and II and their acetates were found to provide direct experimental evidence for the configuration and conformation of isomers I and II.

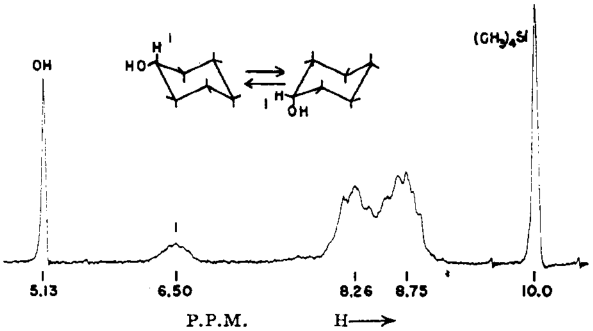


Fig. 1. The proton magnetic resonance of cyclohexanol in carbon tetrachloride at 23° (60 mc.)[8]

Diphenyltin dihydride gave a mixture containing only isomers I and II with approximately 85% I. Isobutylmagnesium bromide yielded a mixture containing slightly less than 50% II, a very small amount of I, some unchanged ketone, and a considerable amount of unidentified substance. Cyclopentylmagnesium bromide gave a mixture of I and II in the ratio of 60% *cis* and 40% *trans*, plus a small amount of unchanged ketone. There was no addition product. The presence of unchanged ketone in the last two reactions is attributed to some enolization of the ketone since unchanged ketone was isolated even upon using a large excess of Grignard reagents. The action of certain organomagnesium halides as reducing agents for aldehydes and ketones is well known,[4] and the stereospecifity of isobutylmagnesium bromide as a reducing agent for certain substituted cyclohexanones has been investigated previously,[5] but there is no evidence of previous investigation of this sterospecificity for cyclopentylmagnesium bromide. Pure II was separated from the mixture of I and II through the separation of the α-naphthylurethans with subsequent reduction with lithium aluminum hydride plus aluminum

---

[1] This investigation was supported by a PHS research grant, No. H-3843 (R1), from the National Heart Institute, Public Health Service. Presented at the 138th Meeting of the American Chemical Society, New York City, N. Y., September 11-16, 1960.

[2] K. D. Hardy and R. J. Wicker, *J. Am. Chem. Soc.*, 80, 640 (1958).

[3] H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, 80, 3798 (1958).

[4] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 153.

[5] P. Anziani, A. Aubry, G. Barraud, M. M. Claudon, and R. Cornubert, *Bul. soc. chim.*, France, 408 (1955).