acid (1.32 g, 0.007 mol) in ethanol (250 ml) was added dropwise over a 1-hr period to a refluxing solution of compound **2** (2.2 g, 0.014 mol) and *p*-toluenesulfonic acid (1.32 g, 0.007 mol) in ethanol (100 ml). The mixture was refluxed for 24 hr and cooled in ice. A small amount of the *p*-toluenesulfonic acid of **2** was separated by filtration and the filtrate was concentrated *in vacuo* to approximately 150 ml and cooled in ice. The precipitate was collected by filtration and washed with ether until all the formed 10-phthaloperinone was removed. Recrystallization of the residue from ethanol yielded 1.6 g (30%) of the *p*-toluenesulfonic acid salt of **11** as bright yellow needles, mp >300°. This salt was neutralized with ammonium hydroxide. Chromatography on alumina of the resulting red solid and recrystallization from dimethylformamide–water gave **11**, mp >300°.

Anal. Calcd for $C_{28}H_{18}N_4$: C, 81.93; H, 4.42; N, 13.65. Found: C, 81.84; H, 4.88; N, 13.47.

Reaction of 1,3-Indandione with Diamine 2. 10-Methyl-10-phthaloperinol (14).—To a refluxing solution of **2** (1.58 g, 0.01 mol) and *p*-toluenesulfonic acid monohydrate (1.9 g, 0.01 mol) in ethanol (100 ml) was added dropwise over 0.5 hr a solution of 1,3-indandione (1.46 g, 0.01 mol) in ethanol (100 ml). The mixture was refluxed for an additional 24 hr, concentrated to *ca.* 50 ml under reduced pressure, and cooled in ice to give 2.7 g (54%) of the *p*-toluenesulfonic acid salt of **14** with ethanol of crystallization as bright red-orange needles, mp 114–124°, with softening and evolution of ethanol. Removal of the ethanol of crystallization was carried out by refluxing a mixture of the above salt (2.7 g) with acetone (250 ml) for 24 hr, collecting the solid by filtration, and washing with acetone. A 62% yield was obtained.

To a slurry of the above *p*-toluenesulfonic acid salt (1.6 g, 0.0035 mol) in water (50 ml) was added concentrated ammonium hydroxide (2 ml); the mixture was allowed to stand for 4 hr. The yellow precipitate collected by filtration, washed with water until free of ammonia, and dried at 60° *in vacuo* gave 1.0 g (100%) of a product which was found identical (mixture melting point, ir, and nmr) with an authentic sample of **14**, prepared from phthalic acid and diamine **2** following the method of Sachs.[15]

Reaction of 1,1-Diphenylacetone with Diamine 2.—A solution of 1,1-diphenylacetone (4.2 g, 0.02 mol) in ethanol (75 ml) was treated with a solution of diamine **2** (3.2 g, 0.02 mol) and *p*-toluenesulfonic acid monohydrate (3.8 g, 0.02 mol) in ethanol (200 ml), following the procedure described above for compound **14**. Upon cooling, 5.7 g (80%) of green platelets was separated and identified as **4a**. The filtrate was evaporated and the dark gummy residue taken up in chloroform and chromatographed on alumina gave diphenylmethane, identified by spectral comparison with an authentic sample.

Registry No.—**2**, 479-27-6; **4a**, 28478-03-7; **4b**, 28478-04-8; **4c**, 28478-05-9; **4d**, 28478-06-0; **4e**, 28478-07-1; **4f**, 2847-08-2; **4g**, 28478-09-3; **4h**, 28537-42-0; **4i**, 28478-10-6; **4j**, 28478-11-7; **5a**, 5157-10-8; **5b**, 28478-13-9; **5c**, 28478-14-0; **5d**, 28478-15-1; **5e**, 28478-16-2; **5f**, 28537-43-1; **5g**, 15666-84-9; **5h**, 25110-47-8; **5i**, 25110-46-7; **5j**, 28478-19-5; **11**, 28478-20-8; **11** *p*-toluenesulfonic acid salt, 28478-21-9.

Acknowledgment.—We gratefully acknowledge the valuable assistance of Dr. Mario F. Sartori in connection with this research.

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Tetrahydroindan Derivatives. Products from the Diels–Alder Condensation of 1-Vinylcyclopentene and *trans*-*o*-Methyl-β-nitrostyrene

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Three isomeric 5-*o*-tolyl-4-nitro- and 4-*o*-tolyl-5-nitro-3a,4,5,6-tetrahydroindans (compounds **1**, **2**, and **3**) were obtained from the Diels–Alder condensation of 1-vinylcyclopentene and *trans*-*o*-methyl-β-nitrostyrene. The presence of the fourth isomer was not detected. Structure assignment was done by nmr.

Vapor phase chromatography (vpc) of the product of the Diels–Alder condensation of *trans*-*o*-methyl-β-nitrostyrene and 1-vinylcyclopentene indicated three components which were designated **1**, **2**, and **3** according to the order of emergence from a QF-1 column. The integrated peaks were in the approximate ratio of 2:1:1, respectively. The products were separated by descending dry column chromatography[2] on silica gel. The presence of the fourth isomer was not detected. The isolated isomers were characterized by nmr to be *trans*-4-nitro-*cis*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (**1**), *cis*-4-*o*-tolyl-*trans*-5-nitro-3a,4,5,6-tetrahydroindan (**2**), and *cis*-4-nitro-*trans*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (**3**).[3] Compound **1** was isomerized to **5** when chromatographed on acid-washed alumina or by treating with base. Compounds **2**, **3**, and **5** were desired as possible intermediates for the preparation of certain cyclopentanohexahydrophenanthridines.

Characterization by nmr was done from the signals of the hydrogens at C-4 and C-5, which are isolated from those of the other alicyclic hydrogens. The signal of the hydrogen on the nitro-bearing carbon is readily recognized because of the large deshielding resulting from the electronegativity and magnetic anisotropy of the nitro group.[4] The signal of the hydrogen on the *o*-tolyl-bearing carbon is also recognizable from other signals, as shown for *trans*-4-nitro-5-*o*-tolycyclohexene-3,3,6,6-d_4 (**6**)[5] (see Table I for chemical shift data). The positions of the substituents, C-4 *vs.* C-5, are readily determined from the multiplicity of the signals. H-4 is adjacent to only two hydrogens and its signal will be either a triplet or a quartet (doublet of doublets), while the signals of H-5 will be more complex because of spin–spin splitting by three adjacent hydrogens. Thus, structures **1** and **3** can be differentiated from their positional isomers **2** and **4**. Differentiation between diastereomers is readily done from the widths of the signals of H-4 and H-5; for example, in isomer **3**, in its most probably conformation, H-4 is axial and coupled with axial H-5 and pseudoaxial H-4a, while in the diastereo-

(1) (a) Public Health Service Predoctoral Fellow 5-F01-GM-34,830; (b) abstracted in part from the Ph.D. dissertation of B. D. Whelton, University of Washington, 1970.

(2) B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).

(3) In the nomenclature adopted the configuration of the substituents (cis or trans) is related to the axial bridgehead hydrogen on C-3a.

(4) (a) A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962); (b) W. F. Trager, F. F. Vincenzi, and A. C. Huitric, *ibid.*, **27**, 3006 (1962); (c) D. B. Roll, B. J. Nist, and A. C. Huitric, *Tetrahedron*, **20**, 2851 (1964).

(5) A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *ibid.*, **19**, 2145 (1963).

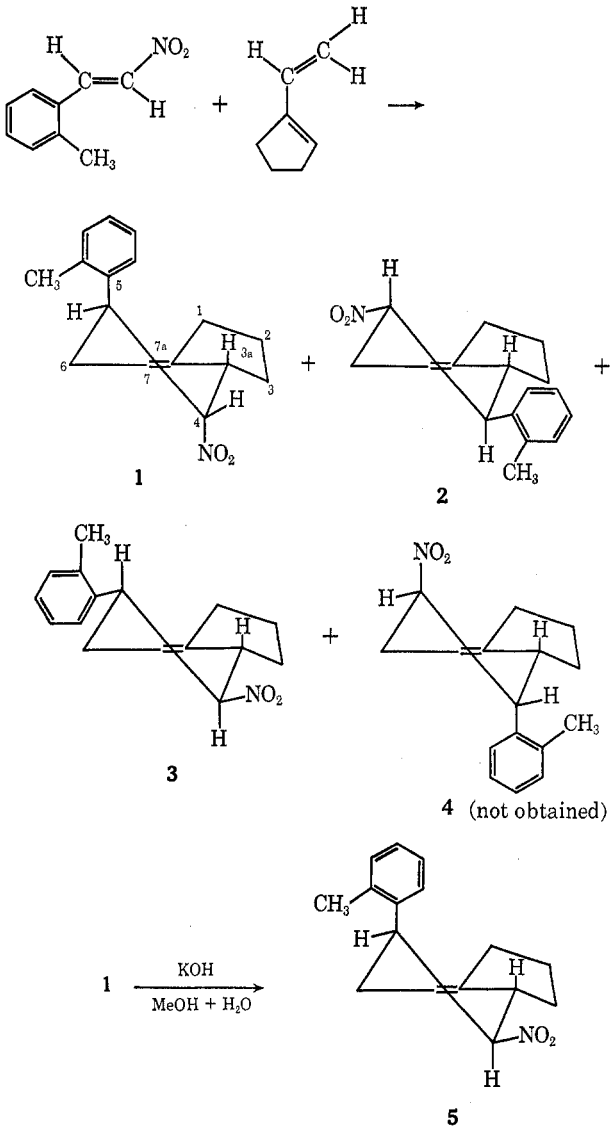

TABLE I

CHEMICAL SHIFT DATA FOR THE 4,5-DISUBSTITUTED 3a,4,5,6-TETRAHYDROINDANS AND RELATED COMPOUNDS[a]

Compd	Solvent	HCNO2	HCPh	Tolyl arom	Tolyl CH3	Vinylic
1	CCl_4	4.83	3.69	7.05	2.39	5.68
2	CCl_4	4.98	3.35	7.09	2.35	5.39
	Pyridine	≃ 5.38	3.43	...	2.38	≃ 5.38
3	CCl_4	4.57	3.71	7.07	2.34	5.45
5	CCl_4	4.40	4.08	7.02	2.15	5.60
6[b]	CCl_4	4.93	3.69	7.10	2.36	5.41
7[c]	CCl_4	4.71	3.40	7.09	2.33	...

[a] Expressed in δ units; TMS used as internal reference. [b] *trans*-4-Nitro-5-*o*-tolylcyclohexene-3,3,6,6-d_4.[5] [c] *trans*-2-*o*-Tolylnitrocyclohexane-3,3,6,6-d_4.[5]

mer **1** H-4 is cis to the bridgehead axial H-3a and can never assume an axial orientation. The sum of J_{43a} and J_{45} will be smaller in **1** than in **3** regardless of the conformation of **1**. Likewise, the sum of the coupling constants of H-5 with the three adjacent hydrogens is larger for **3** than for **1**. Only one half-chair conformation is possible because of the fixed orientation of bridgehead H-3a, but other flexible conformations are not excluded. The same reasoning applies to the relative widths of the signals of H-5 in **1** and **3**. Differentiation

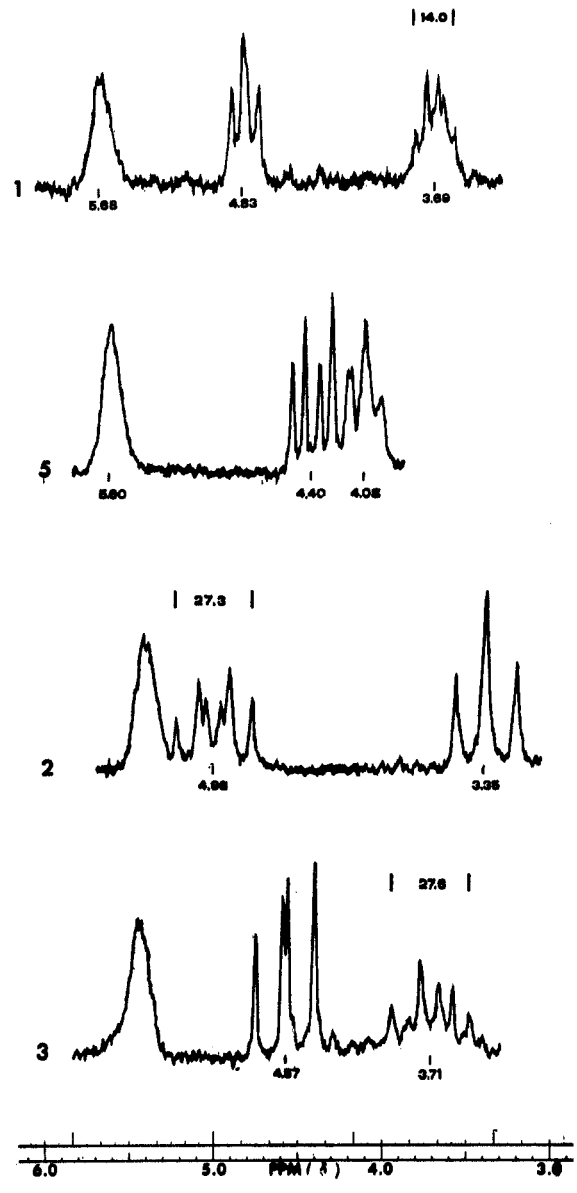

Figure 1.—Portions of 60-MHz nmr spectra of **1**, **5**, **2**, and **3** in carbon tetrachloride. Chemical shifts are in δ units with TMS as internal reference.

between diastereomers **2** and **4** is done in the same manner.

Figure 1 gives the spectra of the signals of H-4, H-5, and H-7 for compounds **1**, **2**, **3**, and **5**. Compound **1** gives spectrum 1. The signal of the hydrogen on the nitro-bearing carbon is at δ 4.83 and that on the tolyl-bearing carbon is at δ 3.69. The relative multiplicity of the two signals establishes that the nitro group is on C-4 and the tolyl group on C-5. The widths of the signals, 9.6 Hz for H-4 and 14.0 Hz for H-5, establish the configuration shown in structure **1**. Analysis of the apparent triplet of H-4 at δ 4.83 shows unequal spacing between peaks and indicates coupling constants of 5.2 and 4.4 Hz for H-4 with H-3a and H-5. Skewness of the signal toward the upfield direction prevents complete resolution of the expected doublet of doublets. A dynamic equilibrium between several conformations is expected but the widths of the signals of H-4 and H-5 suggest that on a time average there is a considerable population of the half-chair conformation depicted in structure **1** with both substituents having essentially

axial orientations. The spectrum of **5**, the compound resulting from epimerization of **1** at C-4, is also very relevant in the characterization of **1**. The signal of H-4 at δ 4.40 is a four-peak multiplet, J_{43a} = 9.8 and J_{45} = 4.4 Hz, and is consistent with H-4 having essentially an axial orientation and being coupled with one axial and one equatorial hydrogen. The signal of H-5 at δ 4.08 has a width of 12.3 Hz and is slightly narrower than in **1**. On the basis of the known J_{54} of 4.4 Hz from the signal of H-4, the splitting pattern of H-5 indicates that H-5 is coupled unequally with the hydrogens on C-6 ($J_{56(axial)}$ = 6.7 and $J_{56(eq)} \simeq$ 1.2 Hz). This indicates that the time average dihedral angle between H-5 and equatorial H-6 is different from that between H-5 and axial H-6. The widths of the signals of H-4 and H-5 indicate that on a time average there is a considerable population of the conformation depicted by structure **5**.

Compound **3** gives spectrum 3. The relative multiplicity of the signals at δ 4.57 and 3.71 establishes that the nitro group is on C-4 and the tolyl group on C-5. The signal of H-4 (doublet of doublets) yields coupling constants of J_{45} = 11.3 and J_{43a} = 9.6 Hz and clearly indicates that H-4 is axial and coupled with two axial hydrogens.[5] The width of the signal of H-5 (δ 3.71) of approximately 27.6 Hz is consistent with H-5 being axial and coupled with two axial and one equatorial hydrogens. The complexity of the signal of H-5 indicates that there is averaging of coupling constants of $J_{56(eq)}$ and $J_{56(axial)}$. Spectrum 3 definitely establishes that **3** is the diastereomer of **1** and that it has the configuration and conformation depicted by structure **3**.

Spectrum 2 establishes that compound **2** has the nitro group on C-5 and the tolyl group on C-4 and that both substituents have the equatorial orientation as depicted in structure **2**. The signal of H-4 at δ 3.35 gives an apparent triplet with slightly unequal spacings, 11.3 and 10.3 Hz. This establishes that H-4 is axial and coupled with two axial hydrogens. The slight difference in spacings indicates a small difference in coupling constants between J_{45} and J_{43a}. The former is probably the largest. Skewness to the right (toward the signal of H-3a) of the expected four-peak multiplet prevents the resolution of the inner components into discrete peaks. The width of the signal of H-5 (27.3 Hz) clearly indicates that H-5 has the axial orientation and is coupled with two axial and one equatorial hydrogens. The complexity of the signal indicates that there is averaging of coupling constants of $J_{56(eq)}$ and $J_{56(axial)}$ resulting from the closeness of chemical shifts of the axial and equatorial hydrogens on C-6. This averaging of coupling constants precludes the determination of coupling constants between H-5 and C-6 hydrogens by first-order approximation, but it does not change the width of the signal of H-5. The sum of the coupling constants is not affected.[6] The observed multiplet is consistent with J_{54} = 11.2 Hz and averaging of coupling constants of axial and equatorial C-6 hydrogens with H-5 to give apparent constants of 8.2 and 8.0. A sum of 16.2 Hz is not unreasonable for the two coupling constants since it has been observed that geminal and vicinal coupling constants of hydrogens on carbons in proximity to an sp^2 hybridized carbon are often increased.[7] The spectrum of **2** was also determined in pyridine, in which case the signal of H-5 overlapped the signal of the vinylic hydrogen at about δ 5.38. The width of the signal was unchanged and the separation of the two outer components was again 8.0 Hz, indicating that the difference in chemical shifts of the two hydrogens on C-6 is still small. The position of the signals of the C-6 hydrogens cannot be determined with certainty. In pyridine the signal of H-4 is shifted to δ 3.43 but is otherwise identical with that in spectrum 2.

(6) (a) W. F. Trager, B. J. Nist, and A. C. Huitric, *Tetrahedron Lett.*, 2931 (1965); (b) W. F. Trager, B. J. Nist, and A. C. Huitric, *J. Pharm. Sci.*, **56**, 698 (1967), and references therein.

Experimental Section

All nmr spectra were recorded on a Varian A-60 spectrometer at *ca.* 37° utilizing ~20% w/v solutions with tetramethylsilane (TMS) as the internal reference. Infrared spectra were determined using a Beckman IR-5-A infrared spectrophotometer. Melting points were determined on the Kofler micro hot stage and are uncorrected. The Aerograph 204 gas chromatograph was employed for all vpc analyses. Elemental analyses were conducted by the Huffman Laboratories, Wheatridge, Colo. The silica gel used was Brinkmann 0.05–0.2 mm (70–325 mesh). For the sake of uniformity and reproducibility, the silica gel was always heated at 120° for 48 hr prior to deactivation. The hexane used for chromatography was purified by shaking with concentrated sulfuric acid and distillation over calcium hydride as the final purification step. Reagent grade carbon tetrachloride was used without purification.

1-Vinylcyclopentene.[8]—1-Ethynylcyclopentanol[9] was reduced to 1-vinylcyclopentanol by the general method of acetylene reduction described by Augustine[10] using 5% palladium on barium sulfate. The product, fractionated with a spinning band column, was found by vpc on QF-1 to contain less than 10% of the saturated alcohol. Dehydration by potassium bisulfate[11] gave 1-vinylcyclopentene of about 90% purity.

***trans*-4-Nitro-*cis*-2-*o*-tolyl-3a,4,5,6-tetrahydroindan (1), *cis*-4-*o*-Tolyl-*trans*-5-nitro-3a,4,5,6-tetrahydroindan (2), *cis*-4-Nitro-*trans*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (3), and *cis*-4-Nitro-*cis*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (5).**—Compounds **1**, **2**, and **3** were synthesized essentially by the methods known for the Diels–Alder condensation of β-nitrostyrenes and butadiene.[4b] A solution of 28.6 g of a mixture of olefins containing at least 90% 1-vinylcyclopentane, 18.37 g (0.112 mol) of *trans*-*o*-methyl-β-nitrostyrene,[4b] 15 ml of toluene, and 50 mg of hydroquinone was heated under nitrogen at 90–95° in a small stainless steel Parr bomb for 4 days. Periodic vpc analysis on a QF-1 column showed the formation of three products which remained in the same ratio of about 2:1:1 throughout the progress of the reaction. Removal of the volatile material yielded an orange-brown oil from which isomers **1**, **2**, and **3** were obtained by a sequence of dry column[2] chromatography procedures. The initial purification was done by placing the content of the readtion mixture (impregnated on some silica gel) on a 4-ft column containing 2000 g of silica gel deactivated with 15% of water (Brockmann Activity III[2]). Elution with 3 l. of 1:19 carbon tetrachloride–hexane solution removed the hydrocarbon materials. The column was next eluted with 3 l. of carbon tetrachloride to give 18.4 g of yellow oil containing **1** in greater amount and **3** in lesser amount. A final elution, with 3 l. of carbon tetrachloride, gave 7.9 g of yellow oil containing **2** in greater amount, some **3**, and small amounts of **1** and of the starting styrene. The final sepration of these mixtures was done by the dry column technique using a 3:2 (by volume) carbon tetrachloride–hexane mixture and 15% water–deactivated silica gel equilibrated with 10% (by weight) of the solvent mixture. Optimal results were achieved when a 4 ft by 46 mm column was used for 3 g of mixture. The separated isomers were treated with decolorizing carbon in hexane.

(7) W. F. Trager and A. C. Huitric, *ibid.*, **56**, 1111 (1967), and references therein.

(8) V. F. Kucherov and E. P. Serebryakov, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, 1057 (1960); *Chem. Abstr.*, **55**, 475 (1961).

(9) O. F. Beumel and R. F. Harris, *J. Org. Chem.*, **29**, 1872 (1964).

(10) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, p 69.

(11) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **20**, 1178 (1955).

Compound **1** failed to crystallize and elemental analysis was obtained on its solid epimer **5** which was obtained by dry column chromatography of **1** on Merck acid-washed alumina (activity II[2]) and carbon tetrachloride or by isomerization of **1** under basic conditions (0.37 equiv KOH) in a 12:1 methanol–water solution. Neutralization of the basic solution with aqueous ammonium chloride solution yielded a mixture of **5** and **1** in a ratio of 7:3 (vpc on QF-1) from which **5** crystallized out in methanol. The isomerization was repeated on the residue.

Compound **2** gave colorless crystals from 2-propanol: mp 95.5–97°; ir (KBr) 1372 and 1540 (NO_2). Compound **3** gave colorless crystals from methanol: mp 91.8–92.2°; ir (KBr) 1378 and 1537 (NO_2). Compound **5** gave colorless crystals from methanol: mp 103.5–104°; ir (KBr) 1355 and 1520 (NO_2).

Anal. Calcd for $C_{16}H_{19}NO_2$: 74.68; H, 7.44; N, 5.44. Found for **2**: C, 74.42; H, 7.63; N, 5.27. Found for **3**: C, 74.29, H, 7.48; N, 5.37. Found for **5**: C, 74.47; H, 7.39; N, 5.21.

Registry No.—**1**, 28638-60-0; **2**, 28638-61-1; **3**, 28638-62-2; **5**, 28638-63-3; 1-vinylcyclopentene, 28638-58-6; *trans*-*o*-methyl-β-nitrostyrene, 28638-59-7.

Unique Formation of a Benzocyclobutene Derivative. The Diazotization of 3-Amino-4-*tert*-butyl-5-nitrobenzoic Acid[1]

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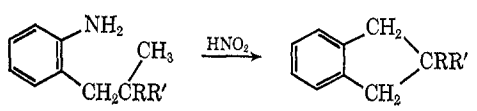
We have observed an unusual ring closure reaction leading to the formation of 1,1-dimethyl-4-carboxyl-6-nitrobenzocyclobutene (**4a**, the major isolated product, 41% crude yield) during the decomposition of the diazonium salt from 3-amino-4-*tert*-butyl-5-nitrobenzoic acid (**3a**). The methyl ester **3b** gave comparable results. This benzocyclobutene derivative was formed in approximately the same yield when the dilute sulfuric acid solution of the diazonium salt was heated (65°), was photolyzed (0°) with ultraviolet light, or was heated (65°) with copper bronze. However, treatment with cuprous bromide in hydrobromic acid gave the normal bromo derivative (47% yield with 44% recovered starting amine); no benzocyclobutene was observed under these conditions. The 1,1-dimethyl-4-carboxyl-6-nitrobenzoic acid was reduced to the corresponding amine which underwent normal diazotization and decomposition of the diazonium compound to give the corresponding phenol.

A recent report by Martinson[2] concerning a reaction leading to the closure of a five-membered ring to give indans (**2**) during deamination of certain *o*-alkylanilines (**1**) has prompted us to publish the following observation encountered during an attempt to synthesize 3-hydroxy-4-*tert*-butyl-5-nitrobenzoic acid.

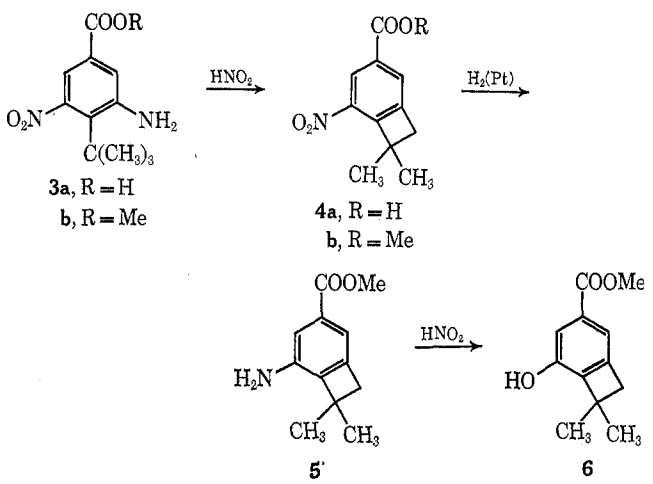
Martinson found indan (**2**, R, R′ = H; 13%), 2-methylindan (**2**, R = H; R′ = Me; 35%), and 2,2-dimethylindan (**2**, R, R′ = Me; 88%) to be formed along with the expected phenol from the diazotization of *o*-propyl-, *o*-isobutyl-, and *o*-neopentylanilines, respectively.



1 **2**

We have found that deamination of the *o*-*tert*-butylaniline derivative **3a** failed to give any appreciable amount of the expected 3-hydroxy-4-*tert*-butyl-5-nitrobenzoic acid; instead, the major product was identified as 1,1-dimethyl-4-carboxy-6-nitrobenzocyclobutene **4a** (41% crude yield, 27% purified yield, isolated as its methyl ester) by its analysis and spectral properties. The deamination of the methyl ester **3b** followed a parallel course. The diazotization was carried out with sodium nitrite in sulfuric acid (nitrosoylsulfuric acid). The decomposition was either done by heating to 65°, by heating to 65° in the presence of copper bronze, or by irradiating at 0° with ultraviolet light (2537 Å, quartz vessel) with no significant change in the yield of the benzocyclobutene **4a**.

The benzocyclobutene structure of this product is derived from the following evidence. The acid **4a** no



3a, R = H
b, R = Me

4a, R = H
b, R = Me

5 **6**

longer shows an nmr signal for a *tert*-butyl group but instead has a singlet δ 1.58 (6 H) assigned to the *gem*-dimethyl protons of the cyclobutene ring. No previous examples of *gem*-dimethylbenzocyclobutenes have been published for comparison, but there is no reason to suppose that the chemical shift for such a signal would differ widely from that of a normal *tert*-butylbenzene derivative; *i.e.*, *p*-*tert*-butyltoluene, δ 1.32; *o*-*tert*-butylnitrobenzene, δ 1.40; 3-amino-4-*tert*-butyl-5-nitrobenzoic acid, δ 1.50; and *o*-*tert*-butylphenol,[3] δ 1.37. The singlet at δ 3.11 (2 H) is assigned to the methylene protons of the cyclobutene ring. This chemical shift is in accord with that reported for the methylene protons of benzocyclobutene itself (δ 3.14)[4a] and compatible with that reported for 1,1-dichloro-3,4,5,6-tetramethylbenzocyclobutene (δ 3.8).[4b] The spectrum shows two signals centered at δ 8.10 (1 H) and 8.70 (1 H) assigned

(1) We gratefully acknowledge support by the National Institutes of Health (NIH RO1GM 16031-09).

(2) P. Martinson, *Acta Chem. Scand.*, **22**, 1357 (1968).

(3) K. C. Dewhirst and C. A. Reilly, *J. Org. Chem.*, **30**, 2870 (1965).

(4) (a) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. I, Interscience, N. Y., 1967, p 203; (b) H. Hart and R. W. Fish, *J. Amer. Chem. Soc.*, **82**, 749 (1960).