polymer. The polymer was purified by dissolution in methanol and reprecipitation from isopropyl alcohol. Repetition of this procedure yielded an analytical sample. The compound was soluble in acetone, chloroform, and acetonitrile.

The infrared absorption spectrum of the polymer showed absorption at 1695, 1718 (shoulder, s), and 1595 cm.$^{-1}$ (s, C=N). The ultraviolet absorption spectrum showed $\lambda_{max}^{CH_3CN}$ 230 mμ (ε 18,130) and 277 (5130).

Anal. Calcd. for $(C_{19}H_{16}N_2O_2S)_n$: C, 67.83; H, 4.79; N, 8.33; S, 9.53. Found: C, 67.63; H, 4.85; N, 8.49; S, 9.45; mol. wt. (T.E.M.), 2300. This corresponds to an average value of *n* as 6.8.

The above reaction was also carried out using methacrylyl chloride in place of acrylyl chloride. However, no characterizable product was obtained.

The infrared spectra of all the compounds were taken in potassium bromide on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer and the nuclear magnetic resonance spectra were determined on a Varian instrument operating at 60 Mc.

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cis Addition of Performic Acid to Indene and Nuclear Magnetic Resonance Spectra of 1,2-Disubstituted Indanes

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The addition of performic acid to indene has been shown to give *cis*-2-formyloxy-1-hydroxyindane (IV). The unexpected location of the formate group at C-2 was proved by chemical and n.m.r. evidence. The conversions of IV, its *trans* isomer (VI), and both *cis*- (I) and *trans*-1,2-dihydroxyindane (III) to 2-indanone by treatment with aqueous acid are discussed and a mechanism is proposed which differs from the mechanism previously proposed. The n.m.r. spectra of fifteen indane compounds are listed, and the data are interpreted in terms of nonplanar five-membered rings.

The addition of performic acid to indene in an aqueous formic acid medium has been found to give two major products, *cis*-1,2-dihydroxyindane (I) and *cis*-2-formyloxy-1-hydroxyindane (IV). Our study of the products from performic acid oxidation of indene stemmed from our interest in the synthesis of 2-indanone oxime and its subsequent reduction[2a] to 2-aminoindane hydrochloride, a potent nonnarcotic analgesic.[2b] Horan and Schiessler[3] recently described the preparation of 2-indanone in high yield by performic acid oxidation followed by dilute sulfuric acid treatment of the intermediate (incorrectly assumed to be 1-formyloxy-2-hydroxyindane). Thin-layer chromatographic examination of samples of the performic acid oxidation reaction showed that indene reacted rapidly with the performic acid to give approximately equal amounts of I and IV, only traces (less than a total of 3–5%) of the corresponding *trans* isomers III and VI, and a small amount of a less polar material (possibly 1,2-diformyloxyindane).[4] Under the reaction conditions, *cis* and *trans* isomers were not equilibrated, so the *cis* products clearly resulted from a *cis* addition rather than from a secondary equilibration. It is not possible to say whether I or IV is the primary product, or whether both products form simultaneously, because equilibration of I and IV occurs fairly rapidly in the reaction mixture.

The addition of deuterium bromide to indene was recently shown by Dewar and Fahey[5] to give 80% *cis*- and only 15–20% *trans*-1-bromo-2-deuterioindane. The proposed mechanism involved formation of an ion pair, consisting of a benzyl-type carbonium ion and a solvated bromide ion, which either collapsed directly to the *cis* adduct or isomerized and then collapsed to the *trans* adduct. The Dewar and Fahey mechanism[5] would predict the unknown *cis*-1-formyloxy-2-hydroxyindane as the primary product of performic acid addition to indene; this predicted product would have to undergo rapid acyl migration to give the isolated ester product (IV). The observed products I and IV cannot be explained by formation of an epoxide and its acid-catalyzed opening to a benzyl-type carbonium ion (or alternatively, attack of OH^+ to give this carbonium ion directly), followed by *cis* attachment of formate ion and subsequent acyl migration, because treatment of 1,2-epoxyindane[6,7] under the conditions of the performic acid oxidation gave a complex mixture of *cis*- and *trans*-disubstituted derivatives. One possible mechanism for the formation of IV is *cis* addition of performic acid to indene, either as a four-centered or as a

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(2) (a) W. E. Rosen and M. J. Green, *J. Org. Chem.*, **28**, 2797 (1963); (b) L. B. Witkin, C. F. Huebner, F. Galdi, E. O'Keefe, P. Spitaletta, and A. J. Plummer, *J. Pharmacol. Exptl. Therap.*, **133**, 400 (1961).

(3) J. E. Horan and R. W. Schiessler, *Org. Syn.*, **41**, 53 (1961).

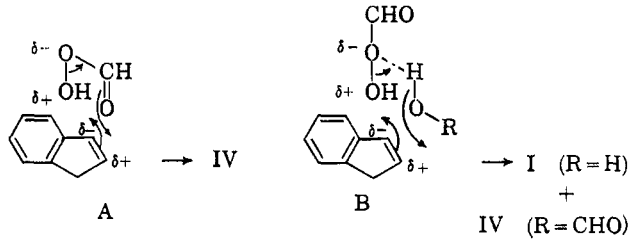
(4) (a) W. Nagata and T. Terasawa [*Chem. Pharm. Bull* (Tokyo), **9**, 745 (1961)] reported the formation of some *cis*-2-benzoyloxy-1-hydroxy product from perbenzoic acid oxidation of 6-methoxy-3,4-dihydronaphthalene. The only *trans* isomer isolated was the *trans*-1-benzoyloxy-2-hydroxy product, presumably resulting from displacement of the intermediate epoxide with benzoate anion at C-1. The authors suggested that the *cis*-2-benzoyloxy-1-hydroxy product resulted from acyl migration of an initially formed *cis*-1-benzoyloxy-2-hydroxy isomer (*not* isolated). (b) After this paper had been submitted for publication, the authors became aware of the report by E. Vogel, W. Frass, and J. Wolpers [*Angew. Chem.*, **75**, 979 (1963)] on the *cis* hydroxylation of dibenzocyclooctatriene with performic acid.

(5) M. J. S. Dewar and F. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2248 (1963).

(6) Originally, there was was some doubt as to whether peracid addition to indene preceded epoxide formation or whether epoxide formation preceded disubstitution [see, for example, J. Böeseken and G. Elsen, *Rec. trav. chim.* **48**, 363 (1929); J. Böeseken and G. C. C. C. Schneider, *J. prakt. Chem.*, **131**, 285 (1931)]. Recent workers have concluded that the epoxide is the initial product [*e.g.*, B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955)] and that disubstituted products result from opening of the epoxide ring [*cf.* R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959)]. Although exceptions to the normal *trans* opening of the epoxide ring have been observed [*e.g.*, C. C. Tung and A. J. Speziale, *J. Org. Chem.*, **28**, 2009 (1963)], such a *cis* opening of 1,2-epoxyindane would be expected to lead to *cis*-1-formyloxy-2-hydroxyindane.

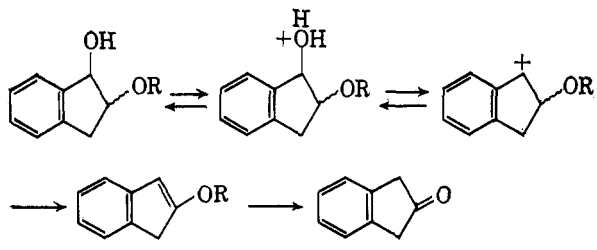
(7) (a) The opening of 1,2-epoxyindane with aqueous acid to give mixtures of *cis*- and *trans*-1,2-dihydroxyindane was reported by Böeseken (ref. 22); (b) H. Bodot, J. Jullien, and E. Leblanc [*Bull. soc. chim. France*, 41 (1962)] described the treatment of 1,2-epoxyindane with hydrogen chloride in dioxane to give 9% 2-indanone, 21% *trans*-1-chloro-2-hydroxyindane, and 64% *cis*-1-chloro-2-hydroxyindane. They attributed the lack of specificity to an intermediate benzyl-type carbonium ion.

six-centered reaction (see structure A). A possible explanation for a simultaneous formation of I and IV is a trimolecular reaction of indene, performic acid, and either water or formic acid (see structure B).



When the performic acid oxidation mixture was held at −15°, a 35% yield of *cis*-2-formyloxy-1-hydroxyindane (IV) was isolated. When heat (steam bath, 1 hr.) was applied, some of the *trans* isomers (VI and III) were generated. Interestingly, the crude reaction mixture, which included *trans* isomers, gave the same yield of 2-indanone on treatment with aqueous sulfuric acid as did pure *cis*-2-formyloxy-1-hydroxyindane (IV). In fact, examination of pure *cis* and *trans* glycols and their corresponding 2-formates (see Table III) showed that each of these components of the crude reaction mixture was converted by aqueous sulfuric acid to 2-indanone at approximately the same rate and in about the same yield.

The mechanism proposed previously[8] for conversion of *trans* glycol (III) to 2-indanone involved prior isomerization to the *cis* glycol (I). This proposal was based in part on the known interconversion of *cis* glycol (I) and *trans* glcyol (III) in aqueous acid,[9] and in part on a consideration of the rates of formation of 2-indanone from I and III. From the similarity in the rates of conversion of the four compounds, I, III, IV, and VI, in strong aqueous acid (see Table III) and from the dependence of the rate of 2-indanone formation on acid concentration (see Fig. 1), we suggest instead that all four compounds are converted to 2-indanone by protonation of the 1-hydroxyl group and elimination of water followed by elimination of a proton and ketonization of the resulting enol or enol ester. The attack of water on the benzyl carbonium ion intermediate, generating either starting material or its 1-epimer, would account for the interconversion of the glycols.



The monoformate product (IV), from performic acid oxidation of indene was shown to be *cis* by saponification to the known *cis*-1,2-dihydroxyindane (I)[9,10] and by formylation of I back to IV. A similar interconversion was carried out between *trans*-2-formyloxy-1-hydroxyindane (VI) and *trans*-1,2-dihydroxyindane (III). As described previously,[9,10] the *cis* glycol (I) but not the *trans* glycol (III) formed an acetonide derivative (II) after short treatment with acetone in the presence of acid catalyst. From the methods of preparation of the compounds (*e.g.*, I from potassium permanganate oxidation of indene[11] and III from aqueous alkaline treatment of 1,2-epoxyindane[10b]) and from their chemical reactions (*e.g.*, I but not III forms an acetonide derivative under mild conditions[10b] and also increases the conductivity of a boric acid solution[10b]), the stereochemical descriptions of both glycols I and III may be considered unambiguous. The position of attachment of the formyl group in compounds IV and VI has been shown by chemical conversions and by interpretations of nuclear magnetic resonance spectra.

Chromic anhydride–pyridine oxidation of IV and of VI gave 2-formyloxy-1-indanone (V) in high (90–100%) yield.[12] The ultraviolet absorption spectrum of V (λ_{max} 248 mμ, ε 13,350) was consistent with those of known 2-substituted 1-indanones. In contrast to the moderate instability of 2-acetoxy-1-indanone,[13] V was quite stable on prolonged standing at room temperature. The 2,4-dinitrophenylhydrazone derivative of V formed readily, and its ultraviolet absorption spectrum (λ_{max} 384 mμ, ε 32,000) confirmed[14] the 2-substituted 1-indanone structure. Short warming of V in aqueous ethanol with semicarbazide hydrochloride and sodium acetate, however, caused hydrolysis of the formate grouping, and gave 2-hydroxy-1-indanone semicarbazone.

An attempt was made to convert IV and VI to 1-methoxy-2-indanone (VIII), in order to provide chemical proof of the C-2 location of the formate groups of IV and VI. The hydroxyl groups at C-1 were etherified with diazomethane in methylene chloride, using fluoboric acid catalyst, giving *cis*-2-formyloxy-1-methoxyindane (VII) from IV and *trans*-2-formyloxy-1-methoxyindane (IX) from VI. Saponification of either VII or IX to the corresponding 2-hydroxy-1-methoxyindane, followed by sodium dichromate oxidation, was expected to give pure VIII. In fact, both VII and IX gave mixtures of products in which VIII was presumably only one component. Attempts to isolate pure VIII by vapor phase chromatography were unsuccessful. The ultraviolet and infrared absorption spectra of the two product mixtures were the same, and ultraviolet absorption intensity measurements suggested that less than 25% of a 1-keto product was present (possibly as a 1,2-diketone[13]). When either product mixture was treated with 2,4-dinitrophenylhydrazine under mild conditions, only the osazone X was isolated. Osazone formation must have resulted either from reaction of indane-1,2-dione in the product mixture, or from oxidation of VIII by 2,4-dinitrophenylhydrazine.[14,15] The isomer of VIII, 2-methoxy-1-indanone, was reported to form its 2,4-dinitrophenylhydrazone derivative without difficulty.[14,16]

(8) C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.*, **62**, 3473 (1940).

(9) P. H. Hermans, *Ber.*, **57**, 824 (1924).

(10) (a) C. van Loon, dissertation; Delft, 1919; (b) C. van Loon, *Koninkl. Akad. Wetenschap. Amsterdam*, **28**, 213 (1919); *Chem. Zentr.*, I, 331 (1920); (c) P. E. Verkade, J. Coops, Jr., C. J. Maan, and A. Verkade-Sandbergen, *Ann.*, **467**, 217 (1928); (d) S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, **75**, 2297 (1953).

(11) F. Heusler and H. Schieffer, *Ber.*, **32**, 28 (1899).

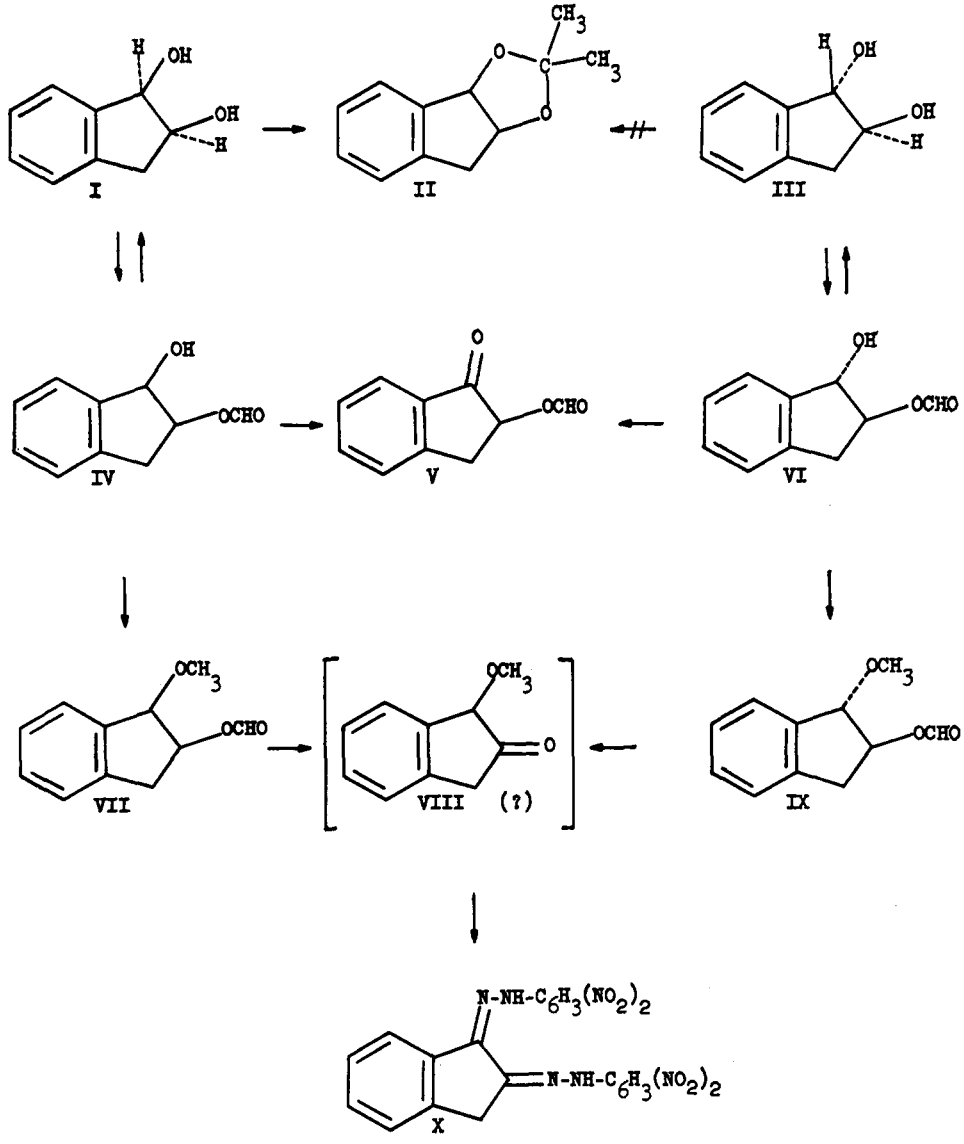
(12) With the *cis* monoformate, this evidence by itself is inconclusive in establishing the location of the formyloxy group, because formyl migration from the C-1 oxygen to the C-2 oxygen followed by oxidative attack on the active benzyl hydrogen would also result in formation of V. Such migration of the formyl group with the *trans* monoformate, however, is less likely.

(13) F. Ishiwara, *J. prakt. Chem.*, **108**, 194 (1924).

(14) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953).

(15) The oxidizing capacity of 2,4-dinitrophenylhydrazine has been discussed by E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1762 (1951).

(16) W. Treibs and W. Schroth, *Ann.*, **639**, 204 (1961).



The chemical evidence from oxidation reactions (to V and VIII), therefore, suggested that the formyloxy group was at C-2. Unambiguous proof of this assignment, however, was obtained only by study of the n.m.r. spectra.

Nuclear Magnetic Resonance Spectra.[17]—In both *cis*- and *trans*-1,2-dihydroxyindanes, the hydrogen at C-1 appeared at the lowest field, followed in turn at higher fields by the hydrogen at C-2 and the two hydrogens at C-3, as expected. The assignments of the formate groups of compounds IV and VI to the C-2 positions were confirmed by the paramagnetic shifts of 64 and 54 c.p.s., respectively, for the C-2 proton signals of the *cis* and *trans* compounds. These values are in agreement with those observed for acylation of secondary alcohols.[18]

The *cis* and *trans* derivatives differed significantly in their spin–spin coupling patterns for the hydrogens at C-3 (see Table I). In the *trans* compounds, these hydrogens were split into an octet (AB of an ABXY type, in which Y has only a minimal influence on AB). In the *cis* compounds, these hydrogens were split into a doublet or into two nearly superimposable doublets between which there was no observable coupling of the AB (C-3) hydrogens. In both *cis* and *trans* derivatives, the C-2 hydrogen signal, although undoubtedly complex, appeared as a quartet having a 1:3:3:1 intensity ratio. This quartet implies that the three hydrogens adjacent to the C-2 hydrogen act as almost equivalent neighbors, all having coupling constants of approximately 5 c.p.s. In both *cis* and *trans* derivatives, the C-1 hydrogen signal appeared as a doublet, having a coupling constant with the C-2 hydrogen of *ca.* 5 c.p.s.

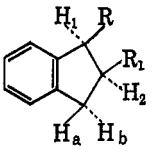
In Table I, the larger coupling constant has been assigned to the C-3 hydrogen (H_b) which is *cis* to the C-2 hydrogen (H_2). This assignment is consistent with the expected difference in dihedral angles between *cis*- and *trans*-related hydrogens (see discussion below). Since the stereochemical structures of the *cis* and *trans* glycols and their derivatives have been proved chemically, the relationship of the hydrogen at C-1 (H_1) to the hydrogen at C-2 (H_2) is known. In a given *cis* compound, the coupling constant between H_1 and H_2 was

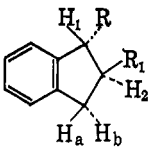
(17) The spectra were obtained with a Varian A-60 spectrometer at 60 Mc./sec. using deuteriochloroform (or pyridine as indicated). All data are reported in cycles per second (c.p.s.) from tetramethylsilane as internal standard. Since the differences in the chemical shifts of the individual protons were large compared with their coupling constants, a first-order treatment (ABX and ABXY) was given to the spectra. The coupling constants for H_1 *cis* and *trans* to H_2, therefore, may be in error by a small amount (*ca.* 1 c.p.s.), but this small error would not affect the conclusions reached.

(18) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, p. 55.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR *cis*- AND *trans*-1,2-DISUBSTITUTED INDANE DERIVATIVES



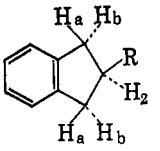


R	R_1		H_a[a]	H_b[a]	H_2[a]	H_1[a]	Other hydrogens[a]
OH	OH	*cis*	175 d (4.4)	177 d (5.2)	259 m	291 d (5.3)	OH 205
		cis[b]	189 d (4.2)	191 d (5 1)	282 m	316 d (5.4)	
		trans[b]	206 q (7.0, 15.7)	183 q (8.2, 15.7)	296 m	333 d (5.6)	
OH	OCHO	*cis*	190 d (3.9)	189 d (5.6)	335 m	314 q (4.9, 7.5)[c]	OH[c] 142 d (7.5), CHO 488
		cis[b]	185 d (4.2)	190 d (6.0)	346 m	330 d (5.1)	
		trans[b]	172 q (5.6, 16.1)	213 q (6.7, 16.1)	350 m	338 d (6.0)	
OCH_3	OCHO	*cis*	188 d (5.6)		335 m	284 d (5.0)	OCH_3 206, CHO 486
		trans	167 q (4.3, 15.9)	211 q (6.9, 15.9)	329 m	286 d (3.3)	OCH_3 208, CHO 480
$OCOCH_3$	OCHO	*cis*	192 d (5.6)	193 d (6.0)	340 m	376 d (5.5)	CH_3CO 124, CHO 485
OH	Br	*trans*[f]	216 q (6.8, 16.2)	190 q (7.6, 16.2)	255 m	318 d (5.5)	OH 156
Br	Br	*trans*[g]	192 q (1.8, 17.7)	228 q (5.0, 17.7)	292[d]	338 d (*ca.* 1)[e]	
OH	NH_2	*trans*[h]	159 q (5.2, 15.9)	185 q (6.2, 15.9)	215 m	285 d (5.4)	OH, NH_2, 153

[a] d = doublet, q = quartet, m = multiplet, ( ) = coupling constant in c.p.s. [b] The solvent was pyridine instead of deuteriochloroform. [c] On addition of D_2O, the hydroxyl doublet was reduced to a singlet and the H_1 quartet became a doublet. [d] The H_2 signal was a doublet and each peak of the doublet was split into a triplet, J = *ca.* 1 c.p.s. [e] The C-3 hydrogens appeared to be long range coupled with the C-1 hydrogen, J = *ca.* 1.5 c.p.s. [f] For preparation, see W. J. Pope and J. Read, *J. Chem. Soc.*, **99**, 2071 (1911); **101**, 758 (1912); and ref. 8. For stereochemistry, see ref. 23. [g] For preparation, see ref. 10d. [h] For preparation, see ref. 1.

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 2-MONOSUBSTITUTED INDANE DERIVATIVES AND FOR 2-FORMYLOXY-1-INDANONE (V)



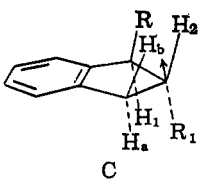
XI

	H_a[a]	H_b[a]	H_2[a]	Other hydrogens
XI, R = NH_2[b]	157 q (5.2, 15.4)	191 q (6.6, 15.4)	228[c]	NH_2 78
XI, R = NH_2[b,d]	158 q (5.8, 15.6)	187 q (6.7, 15.6)	227[c]	NH_2 99
XI, R = $NHCOCH_3$[b]	165 q (5.2, 16.0)	197 q (6.9, 16.0)	280[c]	NH 390
XI, R = $NHOH \cdot H_2O$[b]	167 q (4.8, 16.2)	188 q (5.8, 16.2)	233[c]	
V	187 q (5.3, 17.6)	227 q (7.8, 17.6)	340 dd[e]	CHO 507

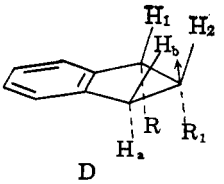
[a] d = doublet, q = quartet, ( ) = coupling constant in c.p.s. [b] See ref. 4. [c] Two overlapping triplets. [d] The solvent was pyridine instead of deuteriochloroform. [e] dd = double doublet.

closer in value to that of H_2 and H_b whereas, in a given *trans* compound, the coupling constant between H_1 and H_2 was closer to that of H_2 and H_a. However, without an unambiguous replacement of one of the C-3 hydrogens by deuterium, these assignments cannot be considered rigorous.

The data can be interpreted in terms of a nonplanar five-membered ring.[19] In the *trans* compounds, a planar ring would give dihedral angles of 120° between H_2 and H_a and of 0° between H_2 and H_b. On the basis of Karplus' values,[20] a difference of *ca.* 4 c.p.s. in spin–spin coupling constants would be expected between such pairs of vicinal hydrogens, the *cis*-related hydrogens having the higher coupling constant. In fact, the difference between these coupling constants is only *ca.* 1–3 c.p.s. Distortion of C-2 from the plane of the five-membered ring, resulting in dihedral angle increases of both the *cis*-related and *trans*-related hydrogens (see structure C), would account for the observed coupling constants. Such increases in dihedral angles would result in a slightly lower coupling constant than expected for the *cis*-related hydrogens and a much higher coupling constant for the *trans*-related hydrogens. The multiplicity of the signals from the C-3 hydrogens in the *trans* compounds and their difference in chemical shift (23–44 c.p.s.) is expected since these hydrogens lie in quite different environments. The striking feature of *cis* compounds is the equivalence or near equivalence in chemical shift of the two C-3 hydrogens. This similarity in chemical shift may be a result of distortion of



C



D

(19) Cyclopentene compounds (including compounds I and III) have been studied experimentally and theoretically by F. V. Brutcher, Jr., and E. L. James [*Dissertation Abstr.*, **24**, 1398 (1963)], who found that puckering of the ring corresponded to a minimum energy conformation.

(20) (a) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963); (b) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). (c) The compounds discussed here are far from ideal. In addition to the strain of the five-membered ring, factors such as altered carbon–carbon bond lengths and the presence of electronegative substituents are hard to evaluate. Hydrogen bonding effects almost certainly influence the structures of hydroxyl-containing compounds. Nevertheless, a neglect of these factors and consideration only of dihedral angles seems to give a simple qualitative interpretation of the data.

C-2 from the plane such that the C-2 substituent exerts nearly identical magnetic anisotropy on both C-3 hydrogens (see structure D). Such a distortion would relieve the steric hindrance of eclipsed functional groups in the *cis* compounds

The n.m.r. spectra described in Table II may also be interpreted in terms of a nonplanar five-membered ring. With the 2-monosubstituted indane compounds, the small difference in coupling constants (1–2 c.p.s.) between *cis*-related and *trans*-related hydrogen pairs was similar to the difference observed in the *trans*-1,2-disubstituted indane compounds. These 2-monosubstituted compounds show octets which differ from those of the C-3 hydrogens in the *trans*-1,2-disubstituted compounds only in that they represent four hydrogens instead of two. The two quartets representing the two H_a hydrogens (*trans* related to H_2) are superimposed, as are also the two quartets representing the two H_b hydrogens. Support for the equivalence of both H_a–H_2 couplings and of both H_b–H_2 couplings was provided by the two nearly superimposable triplets representing the C-2 hydrogen (H_2). The n.m.r. spectrum of 2-formyloxy-1-indanone was also similar to that of the *trans*-1,2-disubstituted indane compounds, having an octet for the C-3 hydrogens and a small difference in the coupling constants between H_2–H_a and H_2–H_b.

Experimental[21]

Preparation of *cis*-2-Formyloxy-1-hydroxyindane (IV) from Indene.[3]—A mixture of 350 ml. of 90% formic acid, 18 ml. of distilled water, and 60 ml. of 35% hydrogen peroxide, added to a 1-l. flask in that order, was stirred and warmed to 35° over 15 min. A total of 58.1 g. (0.50 mole) of indene was added over 2 hr., the reaction temperature being maintained at 35–40° by gentle water cooling. The reaction mixture was stirred at 35° for 1 hr. and then at room temperature overnight. Chilling at −15° for 3 days deposited white needles which were collected and washed with cold ethyl acetate, giving 31.1 g. (35.0%) of *cis*-2-formyloxy-1-hydroxyindane (IV), m.p. 127–130°. One crystallization from ethyl acetate gave 24.0 g. of white needles of IV, m.p. 132–134°; ν_{max} 3235, 3130, 1709, 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}O_3$ (178.19): C, 67.41; H, 5.66; Found: C, 67.54; H, 5.65.

A solution of 5.00 g. of *cis*-2-formyloxy-1-hydroxyindane (IV) in 35 ml. of pyridine was cooled to 0–5° and 4.00 ml. (4.42 g., 100% excess) of acetyl chloride was added dropwise over 15 min. with stirring and cooling. After 1 hr. at 0–5°, the suspension was warmed to room temperature for 1 hr., diluted with 300 ml. of benzene, and washed with water, 1.2 *N* hydrochloric acid, water, 5% aqueous sodium bicarbonate, and water. The solution was dried over anhydrous sodium sulfate, filtered, and stripped to dryness at reduced pressure, leaving 7.80 g. of tacky red solid. Crystallization from isopropyl alcohol (decolorizing with activated charcoal) gave 4.09 g. (69.5%) of orange crystals, m.p. 72–76°. Two additional crystallizations from isopropyl alcohol gave white prisms of 1-acetoxy-2-formyloxyindane, m.p. 74–77°; ν_{max} 1745 (broad), 1238, 1180 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{12}O_4$ (220.23): C, 65.45; H, 5.49. Found: C, 65.57; H, 5.47.

(21) Melting points were determined in an electrically heated aluminum block using open capillaries, and are uncorrected. Ultraviolet absorption spectra were determined in ethanol and infrared absorption spectra were determined as Nujol mulls, unless otherwise specified. Analytical samples were routinely dried *in vacuo* at 75° for 3–5 hr. Thin-layer chromatograms were carried out on silica gel G (E. Merck A. G., Darmstadt) using chloroform–ethyl acetate (1:1) as developing solvent. The plates were of standard thickness (250 μ) and were developed three times (dried between runs), the solvent mixture traveling 15 cm. each time. The *R* (cm.) values (distance traveled inc entimeters after the three developments) were: I, 6.0; II, 13.5; III, 5.0; IV, 11.0; V, 12.5; and VI, 12.0. Nonpolar compounds such as indene, indene oxide, *trans*-2-bromo-1-hydroxyindane, 1-indanone, 2-indanone, and the acetyl derivatives of IV and VI all had values of 13.5–14.0:

Preparation of 2-Indanone from Indene.[3]—The reaction mixture described above in the preparation of *cis*-2-formyloxy-1-hydroxyindane (IV), after standing at room temperature overnight, had a total active oxygen content (hydrogen peroxide plus performic acid plus diformyl peroxide) of 0.10%. Addition of a freshly prepared solution of 10.6 g. of ferrous sulfate heptahydrate in 53 ml. of distilled water reduced the concentration of active oxygen to less than 2 p.p.m.

The dark amber solution was concentrated to 170 ml. (one-third volume) at reduced pressure, diluted with a warm mixture of 140 ml. of concentrated sulfuric acid in 860 ml. of water, and steam distilled. Two liters of steam distillate was extracted with three 100-ml. portions of methylene chloride, and the combined extract was washed once with water and dried over anhydrous sodium sulfate. After filtration, the solution was evaporated at reduced pressure to a light yellow oil which solidified to an off-white crystalline cake of 2-indanone weighing 59.4 g. (90% yield from indene). The 2-indanone may be purified by another

TABLE III

PREPARATION OF 2-INDANONE OXIME FROM 1,2-DISUBSTITUTED INDANES

Starting material	% sulfuric acid (medium[a])	Reflux time (min.)	Yield of oxime (%)[c]
I	25 (A)	30	73.4
	25 (A)	60	75.1
	20 (A)	30	73.9
	20 (A)	60	75.8
	20 (A)	*b*	79.0
III	25 (A)	30	75.3
	25 (A)	60	77.5
	20 (A)	30	73.6
	20 (A)	60	76.5
	20 (A)	*b*	68.9
VI	20 (A)	60	75.8
	20 (A)	*b*	81.1
IV	30 (A)	15	74.8
	30 (A)	30	73.6
	30 (A)	60	70.5
	25 (A)	15	74.8
	25 (A)	30	76.3
	25 (A)	60	75.3
	20 (A)	15	66.4
	20 (A)	30	74.6
	20 (A)	60	77.0
	20 (A)	*b*	78.0
	20 (B)	60	72.7
	20 (B)	*b*	81.9
	15 (A)	15	43.8
	15 (A)	30	60.8
	15 (A)	60	73.1
Crude I and IV	25 (A)	30	66.7
	25 (A)	60	66.0
	25 (B)	30	64.6
	25 (B)	60	59.2
	20 (A)	30	66.7
	20 (A)	60	68.1
	20 (A)	*b*	79.6
	20 (B)	30	66.7
	20 (B)	60	66.0
	20 (B)	*b*	77.0

[a] A = water medium, B = water–formic acid (6:1) medium. [b] Direct steam distillation over 1 hr. [c] Oxime was obtained as follows: 50 ml. of a preheated aqueous acid solution was added to 28.1 mmoles of starting material (*e.g.*, 4.21 g. of I or 5.00 g. of IV), and the mixture was refluxed for the specified time. After the mixture was rapidly cooled in an ice bath, it was extracted with four 20-ml. portions of methylene chloride. The combined extract was washed with water, dried, and concentrated at reduced pressure; the 2-indanone was removed by steam distillation. The work-up of the steam distillate by extraction, and the conversion of the extracted 2-indanone to oxime, is described in detail elsewhere in the Experimental section.

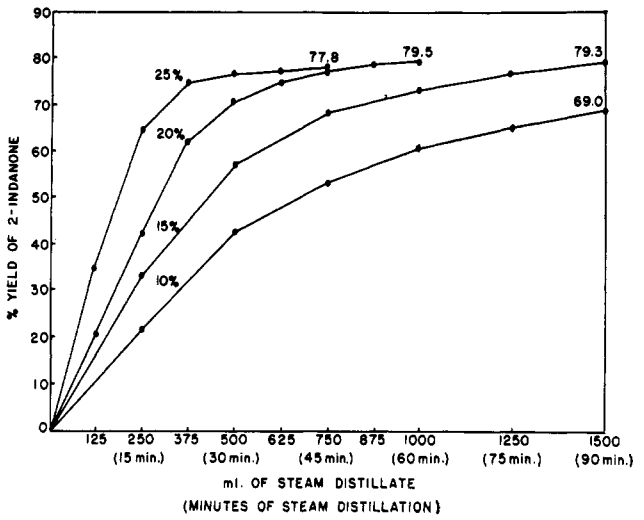


Fig. 1.—Rates of formation of 2-indanone by steam distillation from crude I and IV using different concentrations of sulfuric acid (in water–formic acid, 6:1); yields of 2-indanone are based on starting indene.

steam distillation (allowing pure 2-indanone to crystallize from the distillate) or it may be used directly for preparation of derivatives. Purified 2-indanone had m.p. 57–59°, lit.[3] m.p. 57–58°; ν_{max} 1740 cm.$^{-1}$; λ_{max} 261 mμ (ε 735), 268 (1050), 275 (1100), 296 (sh, 58).

The preparation of 2-indanone oxime from crude 2-indanone, by the method described previously,[1] gave an 85% yield of oxime, m.p. 154–155°. The yellow-orange 2-indanone 2,4-dinitrophenylhydrazone had m.p. 198–198.5°; $\lambda_{max}^{diglyme}$ 250–261 mμ (plateau, ε 12,120), 267 (12,060), 275 (sh, 10,430), 362 (23,390).

Anal. Calcd. for $C_{15}H_{12}N_4O_4$ (312.29): C, 57.69: H, 3.87; N, 17.94. Found: C, 57.80; H, 3.96; N, 17.63.

For comparison purposes, a sample of 1-indanone [m.p. 42–45°; $\nu_{max}^{CHCl_3}$ 1708, 1620 cm.$^{-1}$; λ_{max} 242–243 mμ (ε 12,890), 286–289 (2700), 291–292 (2720)] was converted to its orange-red 2,4-dinitrophenylhydrazone derivative, m.p. 257–258°; $\lambda_{max}^{diglyme}$ 298 mμ (sh, ε 8630), 312 (6820), 387 (31,310); lit.[14] $\lambda_{max}^{CHCl_3}$ 386 mμ (ε 30,200).

Anal. Calcd. for $C_{15}H_{12}N_4O_4$ (312.29): C, 57.69: H, 3.87; N, 17.94. Found: C, 57.76; H, 4.12; N, 17.90.

Preparation of *cis*-1,2-Dihydroxyindane (I) from *cis*-2-Formyloxy-1-hydroxyindane (IV).—A solution of 5.00 g. of *cis*-2-formyloxy-1-hydroxyindane (IV) in 17 ml. of ethanol and 17 ml. of 6 *N* aqueous sodium hydroxide was refluxed for 2.5 hr. The yellow solution was extracted with five 40-ml. portions of ether, and the combined extract was dried over anhydrous potassium carbonate. The filtered solution was stripped to dryness, leaving 4.14 g. (98.3%) of *cis*-1,2-dihydroxyindane, m.p. 94–97°. One crystallization from ethyl acetate raised the melting point to 99–101°, whereas one crystallization from toluene raised the melting point to 107–110° (two crystalline forms, m.p. 101° and m.p. 108°, have been reported[10c,22]), ν_{max} 3240–3340 cm.$^{-1}$.

A 1.00-g. sample of I in 20 ml. of acetone containing 0.5% sulfuric acid was heated on the steam bath for 5 min., cooled to room temperature, diluted with 100 ml. of benzene, and washed well with water, aqueous sodium bicarbonate, and water. The dried benzene solution was stripped to dryness at reduced pressure, leaving 1.22 g. (96%) of *cis*-1,2-dihydroxyindane acetonide (II), m.p. 69–72°. One crystallization from methanol–water gave white crystals, m.p. 70–71°, whose infrared spectrum showed no hydroxyl bands; ν_{max} 1260, 1210, 1052 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.31; H, 7.27.

A stirred solution of 1.00 g. of *cis*-1,2-dihydroxyindane (I) in 30 ml. of pyridine was cooled to 5° and treated dropwise over 1 hr. at 5–10° with a previously prepared and cooled mixture of 20 ml. of formic acid (98–100%) and 8 ml. of acetic anhydride. After 30 more min. at 5–10°, the reaction mixture was allowed to stand overnight at room temperature, cooled, and diluted with 20 ml. of water. After 4 hr., the clear solution was further diluted with 150 ml. of water and was extracted with four 25-ml. portions of methylene chloride. The combined extract was washed free of pyridine with dilute hydrochloric acid washes, and the sodium sulfate dried solution was stripped to dryness at reduced pressure, leaving 1.29 g. of a white solid residue, m.p. 65–108°. Crystallization from ethyl acetate gave a first crop of 0.11 g. (9.3%) of white crystalline *cis*-2-formyloxy-1-hydroxyindane, m.p. 128–128.5°, no depression of melting point when mixed with authentic IV; the infrared spectrum was identical with that of authentic IV.

Anal. Found: C, 67.39; H, 5.78.

Preparation of *trans*-1,2-Dihydroxyindane (III) from *trans*-2-Bromo-1-hydroxyindane.[23]—A suspension of 41.2 g. of *trans*-2-bromo-1-hydroxyindane[8] in a solution of 48.4 g. of sodium carbonate in 725 ml. of water was stirred and refluxed for 3 hr., with a stream of nitrogen bubbling through the suspension. The hot reaction mixture was filtered, and the yellow filtrate was allowed to stand at room temperature overnight. The light brown solid was collected and dried *in vacuo* at 60°, and the 11.3 g. of crude material was thoroughly stirred with toluene, giving 9.2 g. (31.8%) of *trans*-1,2-dihydroxyindane (III), m.p. 157–159°. Crystallization from ethyl acetate gave 8.0 g. (27.7%) of white solid III, m.p. 160–163°, ν_{max} 3130–3210 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}O_2$ (150.18): C, 71.98; H, 6.71. Found: C, 71.68; H, 6.83.

Treatment of the acid-sensitive *trans*-1,2-dihydroxyindane (III) with 0.5% sulfuric acid in acetone (the same conditions under which the *cis* isomer I gave a 96% yield of acetonide, heat for 5 min.) resulted in the recovery of 61% crude III.

Preparation of *trans*-2-Formyloxy-1-hydroxyindane (VI) from *trans*-1,2-Dihydroxyindane (III).—A fine powder of 50.0 g. of *trans*-1,2-dihydroxyindane (III) in 750 ml. of 85% formic acid was stirred at 0–5° for 1 hr. and then stored at −20°. The monoformate VI deposited steadily, affording 15.6 g. (26%) of white solid, m.p. 139–140°, after 24 hr., and a total of 37.5 g. (63.2%) of white solid, m.p. 138–139°, after 4 months. A crystallization from ethyl acetate, followed by a crystallization from methanol–isopropyl alcohol, raised the melting point to 141–143°; ν_{max} 3270, 3170, 1731, 1239 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}O_3$ (178.19): C, 67.41; H, 5.66. Found: C, 67.40; H, 5.79.

Saponification of *trans*-2-formyloxy-1-hydroxyindane (VI) under the conditions described for converting IV to I (except that the *trans* glycol was extracted from the aqueous solution by ether continuously in a liquid–liquid extractor over 2 days) gave 87.0% *trans*-1,2-dihydroxyindane, m.p. 159–161°. One crystallization gave pure III, which had a melting point and mixture melting point with authentic III of 160–163°, and whose infrared spectrum was identical with that of authentic material.

Preparation of 2-Formyloxy-1-indanone (V) from *cis*-2-Formyloxy-1-hydroxyindane (IV).—To a thick yellow suspension of 4.00 g. of chromic anhydride in 40 ml. of dry pyridine was added 4.00 g. of *cis*-2-formyloxy-1-hydroxyindane (IV) at room temperature with stirring. The brown suspension was stirred overnight at room temperature, filtered (insolubles washed well with pyridine), diluted with 200 ml. of benzene, and washed free of pyridine with cold 6 *N* hydrochloric acid. The benzene solution was further washed with water and aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. The filtered solution was stripped to dryness at reduced pressure, leaving 3.55 g. (89.9%) of a pale green oil which crystallized on standing at 5°, m.p. 62–66°. Recrystallization from isopropyl alcohol followed by recrystallization from methanol–water gave 2.42 g. of colorless long needles of 2-formyloxy-1-indanone (V), m.p. 65–68°; λ_{max} 248 mμ (ε 13,350), 292 (2600); ν_{max} 1736, 1715, 1160 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_8O_3$ (176.17): C, 68.18; H, 4.58. Found: C, 68.30; H, 4.75.

The 2,4-dinitrophenylhydrazone derivative had m.p. 232–234° dec.; $\lambda_{max}^{diglyme}$ 267 mμ (sh, ε 11,460), 302 (sh, 4930), 316 (4510), 385 (29,460).

Anal. Calcd. for $C_{16}H_{12}N_4O_6$ (356.30): C, 53.94; H, 3.39; N, 15.73. Found: C, 54.25; H, 3.59; N, 15.99.

Preparation of 2-Hydroxy-1-indanone Semicarbazone from 2-Formyloxy-1-indanone (V).—To a warm solution of 0.25 g. of 2-formyloxy-1-indanone in 0.5 ml. of 95% ethanol and 0.5 ml. of water was added 0.20 g. of semicarbazide hydrochloride and 0.30 g. of sodium acetate. The mixture was warmed in boiling water for 1 min. and then cooled in an ice bath, to give 0.13 g. (39%) of a white solid, m.p. 175–178°. One crystallization from ethanol–water gave the semicarbazone, m.p. 183–185°; λ_{max}

(22) J. Böeseken, *Rec. trav. chim.*, **47**, 683 (1928).

224 mμ (ε 12,760), 231 (sh, 9150), 273 (16,220), 282 (17,470), 299 (17,330), 311 (16,080).

Anal. Calcd. for $C_{10}H_{11}N_3O_2$ (205.22): C, 58.53; H, 5.40; N, 20.48. Found: C, 58.37; H, 5.46; N, 20.50.

Preparation of 2-Formyloxy-1-indanone (V) from *trans*-2-Formyloxy-1-indanone (IV).—Oxidation of *trans*-2-formyloxy-1-hydroxyindane (VI) with chromic anhydride in pyridine under the same conditions as that described above for the *cis* isomer (IV) gave a 98.4% yield of crude V, m.p. 61–64°. One crystallization from isopropyl alcohol gave a 76.6% yield of V, identical with that prepared from the *cis* isomer, m.p. 63–67°; λ_{max} 248 mμ (ε 12,900), 293 (2450); same infrared spectrum as V from IV. The 2,4-dinitrophenylhydrazone derivative had m.p. 239–240°; $\lambda_{max}^{diglyme}$ 266 mμ (sh, ε 12,500), 302 (sh, 5490), 317 (4980), 384 (32,000); same infrared spectrum as the derivative prepared using V from IV.

Anal. Found: C, 54.22; H, 3.41; N, 15.86.

Preparation of *cis*-2-Formyloxy-1-methoxyindane (VII) from *cis*-2-Formyloxy-1-hydroxyindane (IV).—A solution of 5.00 g. of *cis*-2-formyloxy-1-hydroxyindane (IV) in 400 ml. of methylene chloride was cooled to 0–5°, and 0.40 ml. of fluoroboric acid (purchased from the General Chemical Division of Allied Chemical Corp.; material nominally 48–50% was concentrated at reduced pressure to 62–64%, calculated by weight loss) was added. A cold solution of diazomethane was prepared by adding 17.0 g. of N-nitroso-N-methylurea over 45 min. to a stirred mixture of 32.0 g. of 50% potassium hydroxide solution and 200 ml. of methylene chloride at 0 to −10°, diluting with 100 ml. of ice-cold water, and drying the methylene chloride layer over potassium hydroxide pellets for 30 min. The cold diazomethane solution was added over 45 min. to the stirred solution of IV at 0–5°, and the solution was maintained at 0–5° for an additional 1.5 hr. The reaction mixture was washed with water, aqueous sodium bicarbonate, and water, dried over anhydrous sodium sulfate, filtered, and stripped to dryness. The 5.78 g. of yellow oil, which solidified when stored at −15°, was dissolved in 15 ml. of isopropyl alcohol at room temperature and the solution was treated with decolorizing charcoal, filtered, and chilled at −15° to give 1.63 g. (30.5%) of VII, m.p. 62–64°. One recrystallization from methanol–isopropyl alcohol gave fine white needles, m.p. 62–64°, which showed no hydroxyl absorption in the infrared, ν_{max} 1710 and 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}O_3$ (192.22): C, 68.74; H, 6.29. Found: C, 68.54; H, 6.32.

Preparation of *trans*-2-Formyloxy-1-methoxyindane (IX) from *trans*-2-Formyloxy-1-hydroxyindane (VI).—Methylation of 10.0 g. of VI was carried out with diazomethane in cold methylene chloride using fluoroboric acid catalyst, as described above for methylation of the *cis* isomer (IV). The crude reaction mixture, after washing, drying, and evaporating to dryness, gave 12.41 g. of yellow oily residue which was crystallized from petroleum naphtha (b.p. 60–90°) to give 9.16 g. (84.8%) of off-white platelets of IX, m.p. 51–52.5°. The analytical sample was prepared by one additional crystallization from petroleum naphtha, and had m.p. 52–54°, no hydroxyl band in the infrared, ν_{max} 1704 and 1192 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}O_3$ (192.22): C, 68.74; H, 6.29. Found: C, 68.99; H, 6.26.

Preparation of 1-Methoxy-2-indanone (VIII) from *cis*-2-Formyloxy-1-methoxyindane (VII).—A solution of 1.00 g. of *cis*-2-formyloxy-1-methoxyindane (VII) in 4.0 ml. of anhydrous ethanol and 3.2 ml. of 6 *N* aqueous sodium hydroxide was refluxed for 1 hr. The cooled solution was extracted with three 25-ml. portions of ether, and the combined ether extract was washed with water, dried over anhydrous sodium sulfate, filtered, and stripped to dryness, to give 0.84 g. (99%) of a pale yellow-green oil, whose infrared spectrum (liquid) showed a strong broad hydroxyl band (*ca.* 3440 cm.$^{-1}$) but no carbonyl band. The intermediate *cis*-2-hydroxy-1-methoxyindane was dissolved in 1.3 ml. of benzene, cooled to 0–5°, and treated with a cold solution of 0.84 g. of sodium dichromate dihydrate in 2 ml. of glacial acetic acid. The brown reaction mixture was allowed to stand at 0–5° for 2 days, diluted with 25 ml. of water, and extracted with three 25-ml. portions of benzene. The combined benzene extract was washed three times with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness at reduced pressure, leaving 0.63 g. (75%) of crude 1-methoxy-2-indanone (VIII) as a pale yellow-green oil; λ_{max} 238 mμ (ε 3100), 271 (1480) 290 (sh, 540). The infrared spectrum (liquid) showed strong carbonyl absorption at 1723 cm.$^{-1}$ (plus a shoulder at 1700 cm.$^{-1}$) and only weak absorption in the 3400-cm.$^{-1}$ region.

A solution of 0.55 g. of 2,4-dinitrophenylhydrazine in 1.2 ml. of concentrated sulfuric acid, 2.8 ml. of water, and 8.2 ml. of methanol was added to a solution of 0.40 g. of crude 1-methoxy-2-indanone (VIII) in 2 ml. of methanol at room temperature. A yellow-orange solid formed immediately, and, after 15 min. of stirring and 5 min. of cooling, the solid was collected, washed first with cold methanol and then with cold water, and dried *in vacuo* at 60°, giving 0.31 g. of material, m.p. 106–108.5°. Crystallization from ethyl acetate afforded 0.08 g. (6%) of orange crystals, m.p. 203–204° dec.; $\lambda_{max}^{diglyme}$ 257 mμ (sh, ε 16,150), 375 (48,100).

Anal. Calcd. for $C_{21}H_{14}N_4O_8$ (506.39): C, 49.80; H, 2.79; N, 22.13. Found: C, 49.35; H, 3.19; N, 21.71.

Preparation of 1-Methoxy-2-indanone (VIII) from *trans*-2-Formyloxy-1-methoxyindane (IX).—A solution of *trans*-2-formyloxy-1-methoxyindane (IX) in aqueous ethanolic sodium hydroxide was treated as described above for saponification of the *cis*-2-formyloxy isomer (VII) to the *cis*-2-hydroxy isomer. Evaporation of the ether extracts left a quantitative yield of *trans*-2-hydroxy-1-methoxyindane (broad strong hydroxyl absorption in the infrared at 3340–3400 cm.$^{-1}$, but no carbonyl absorption) as a pale green oil. Oxidation of the oily intermediate with sodium dichromate dihydrate, as described above for the *cis* isomer, gave a 74% yield of crude 1-methoxy-2-indanone (VIII) as a pale green oil; λ_{max} 237 mμ (ε 2840), 271 (1370). The oil had an infrared spectrum (liquid) which was the same as that of the oil formed from the *cis* isomer VII, and like the oil from the *cis* isomer it gave with 2,4-dinitrophenylhydrazine a small amount of orange solid, m.p. 199–200°; $\lambda_{max}^{diglyme}$ 257 mμ (sh, ε 23,200) and 374 (45,700), same infrared spectrum.

Anal. Found: C, 49.80; H, 3.49.

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