Chromosorb W DMCS-AW (100°). The retention times (minutes) for each compound are given in the brackets following each compound in the order (A, B): *cis*-1-bromopropene (8.3, . . .), *trans*-1-bromopropene (9.0, . . .), 1-bromopropane (9.7, . . .), 1,1-dibromopropane (41.7, 34.3), 1,1-dibromopropane (44.7, 36.5), *cis*-3-bromo-3-hexene (47.2, 40.3), *trans*-3-bromo-3-hexene (41.7, 44.8).

Product Identification.—All of the products were collected by preparative glpc. *cis*- and *trans*-1-bromopropene were identified by infrared spectral comparison with authentic samples synthesized from 1,2-dibromopropane.[24] 1-Bromopropane was identified by infrared spectral comparison with commercial 1-bromopropane (MC and B). Infrared analysis of authentic bromocyclopropane[25] demonstrated that it was not present in the 1-bromopropane fraction although the retention times of these compounds were identical. Bromocyclopropane in a yield of >1% of the total 1-bromopropane would have been detected. 1,1-Dibromopropene was characterized from its spectral data: infrared, 6.15 μ (C=C); nmr, δ 1.87 (doublet, 3 H, J = 7 cps), 6.17 (quartet, 1 H, J = 7 cps); mass spectrum (70 eV), *m/e* 198 (P), 200 (P + 2), 202 (P + 4); relative intensities to parent peak were 192 and 94%, respectively. 1,1-Dibromopropane was characterized by infrared spectral comparison with an authentic sample obtained from the reaction of bromine with diazopropane; nmr δ 1.41 (triplet, 3 H, J = 7 cps), 2.72 (multiplet, 2 H), 6.13 (triplet, 1 H, J = 6 cps). *cis*-3-Bromo-3-hexene was identified by infrared spectral comparison with an authentic sample.[26] *trans*-3-Bromo-3-hexene was identified by its infrared, nmr, and mass spectral data: infrared, 6.05 μ (C=C); nmr, δ 0.91 (multiplet, 6 H), 2.17 (multiplet, 4 H), 5.55 (triplet, 1 H, J = 6.5 cps); mass spectrum (70 eV), *m/e* 162 (P), 164 (P + 2), intensity of P + 2 relative to P was 96.5%. The nmr spectrum was very similar to that of *trans*-3-iodo-3-hexene.[26]

Attempted Trapping of α-Bromodiazopropane with Acetic Acid.—The reaction of *t*-butyl hypobromite (2.5 × 10⁻² mol) with diazopropane (3.9 × 10⁻¹ mol) at −100° was carried out in the usual manner. A solution of acetic acid (4.3 × 10⁻¹ mol) in Freon 11 was then added dropwise at −100°. The solution became colorless near the end of the addition. Removal of solvent using a rotary evaporator left a red-brown oil possessing the odor of bromine and acetic acid. An nmr of this oil showed the presence of acetic acid and *n*-propyl acetate. A very weak resonance signal at δ 5.75 indicated the possible presence of α-bromopropyl acetate. The chloromethylene protons of chloromethyl acetate give a signal at δ 5.63. Attempts to distil this oil at reduced pressure resulted in decomposition.

Registry No.—*t*-Butyl hypobromite, 1611-82-1; 2, 764-02-3; α-bromopropylidene, 19807-22-8.

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[24] (a) M. S. Kharasch and C. F. Fuchs, *J. Amer. Chem. Soc.*, **65**, 504 (1943); (b) R. C. Neuman, Jr., and D. N. Roark, *J. Mol. Spectrosc.*, **19**, 421 (1966).

[25] E. Renk, R. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 1987 (1961).

[26] (a) Spectral data kindly furnished by Professor G. Zweifel; (b) G. Zweifel and C. C. Whitney, *ibid.*, **89**, 2753 (1967).

Conformations of 1,2-Disubstituted Indans. Electronegativity Corrections to Nuclear Magnetic Resonance Coupling Constants

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Nmr spectra of hydrogens on the cyclopentene rings of 23 1,2-disubstituted indans of known stereochemistry have been analyzed completely. Constants in the Karplus equation that relates vicinal coupling constants to substituent electronegativity have been evaluated using data from the bicyclo[2.2.1]heptene system, and the resulting equations were used to correct the indan vicinal coupling constants for electronegativity effects. The corrected coupling constants (J^u values), which should be a function of dihedral angle only, show that 1,2-disubstituted indans exist as a mixture of two puckered conformations. For both *cis* and *trans* compounds the degree of pucker is controlled by substituent size and not by dipole–dipole forces. In the *trans* compounds the population of the diaxial conformation increases relative to that of the diequatorial conformation as the size of the substituents increases. *trans* compounds bearing a hydroxy group at C_1 or C_2 shown an unusually strong preference for the diequatorial conformation. Analysis of data in the literature shows that 1-haloindans prefer the conformation in which the halogen atom is axial.

Recently conformations of five-membered rings, especially cyclopentanes, have been the subject of a number of studies.[1] Cyclopentene and its derivatives have received less attention. Rathjens, using microwave spectroscopy, concluded that cyclopentene is puckered with an angle of 22° between the skeletal planes,[2] and Jakobsen[3] has interpreted the nmr spectrum of *cis*-3,5-dibromocyclopentene in terms of a ring puckered in the vicinity of 20°. Sable, *et al.*, have also studied substituted cyclopentenes by nmr spectroscopy.[1b] Jackson, *et al.*,[4] have studied some 2-substituted indans and their chromium tricarbonyl complexes, while Rosen, *et al.*,[5] investigated a series of 1,2-disubstituted and 2-substituted indans. Both of the latter groups interpreted their results in terms of a nonplanar cyclopentene ring, but Merritt and Johnson[6] have suggested nearly planar conformations for some fluorinated indans. Vicinal coupling constants in 1,2-disubstituted indans varied erratically with substituent changes and were not reliable indicators of stereochemistry. This work is an effort to identify the factors which determine conformation in 1,2-disubstituted indans and to make a start on the problem of separation of conformational and electronegativity influences on vicinal nmr coupling constants in flexible systems.

Synthesis.—Most 1,2-disubstituted indans used in this work were of well-established stereochemistry or

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[1] (a) H. R. Buys, C. Altona, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **87**, 53 (1968), and previous papers in this series; (b) H. Z. Sable, W. M. Ritchey, and J. E. Nordlander, *Carbohyd. Res.*, **1**, 10 (1965); *J. Org. Chem.*, **31**, 3771 (1966); (c) L. E. Erickson, *J. Amer. Chem. Soc.*, **87**, 1867 (1965); (d) D. J. Pasto, F. M. Klein, and T. W. Doyle, *ibid.*, **89**, 4369 (1967).

[2] G. W. Rathjens, Jr., *J. Chem. Phys.*, **36**, 2401 (1962); see also F. V. Brutcher and E. L. James, *Dissertation Absts.*, **24**, 1398 (1963).

[3] H. J. Jakobsen, *Tetrahedron Lett.*, 1991 (1967).

[4] W. R. Jackson, C. H. McMullen, R. Spratt, and P. Blandon, *J. Organometal. Chem.*, **4**, 392 (1965).

[5] W. E. Rosen, L. Dorfman, and M. R. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

[6] R. F. Merritt and F. A. Johnson, *ibid.*, **31**, 1859 (1966).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF *cis*-1,2-DISUBSTITUTED INDANS[a,b,o]

Compd	R_1	R_2	J_{12} (Hz)	J_{23} (Hz)	J_{24} (Hz)	H_1 (Hz)	H_2 (Hz)	H_3 (Hz)	H_4 (Hz)	Other	RMS[q] error	Solvent
1	OH	OH	5.1	(7.4)	2.0[p]	294.2	236.2	177.9	173.4	*g*	0.09	*c*
2	OCH_3	OCH_3	4.9	7.3	6.6	269.0	233.9	178.3	173.1	*h*	0.05	*d*
3	$OCOCH_3$	$OCOCH_3$	5.4	(6.8)	5.6	364.9	323.5	185.9	180.9	*i*	0.05	*c*
4	Acetonide		5.6	6.5	0.5	329.0	296.4	187.2	181.9	*j*	0.07	*c*
5	Carbonate		6.7	6.4	1.2	362.5	329.4	203.0	194.2		0.03	*c*
6	OH	OCHO	4.9			325	338	191	186	*k, l*		*e*
7	$OCOCH_3$	OCHO	5.4	7.4	4.4[p]	372.2	331.1	193.2	187.4	*m*	0.08	*d*
8	OH	Cl	5.1	(5.5)	3.5[p]	307.2	283.3	197.5	188.0	*k*	0.10	*c*
9	$OCOCH_3$	Cl	5.2	6.8	4.5[p]	359.8	279.7	191.7	190.1	*n*	0.05	*d*
10	Cl	Cl	5.1	(8.8)	5.1[p]	303.1	257.2	182.3	180.9		0.10	*f*
11	Br	Br	5.0			311						*f*

[a] Chemical shifts are in hertz downfield from internal tetramethylsilane at 60 MHz and coupling constants and root mean square error are in hertz. [b] All compounds gave a complex multiplet at 420 to 450 Hz for the aromatic hydrogens. [c] Acetone-d_6. [d] Carbon tetrachloride. [e] Pyridine. [f] Neat liquid. [g] OH at 240 Hz. [h] Methoxys singlet at 197 Hz. [i] Acetoxy methyls at 117 and 118 Hz. [j] Methyl singlets at 66 and 80 Hz. [k] Trace of HCl gas added, OH signal not determined. [l] Aldehyde hydrogen singlet at 505 Hz. [m] Acetoxy methyl 124 Hz, aldehyde hydrogen 487 Hz. [n] Acetoxy methyl 122 Hz. [o] Values in parentheses have probable errors greater than 1 Hz. [p] $0.3 <$ probable error $\leqslant 0.2$ Hz. [q] Root mean square.

TABLE II

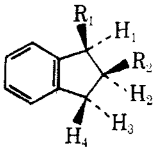
CHEMICAL SHIFTS AND COUPLING CONSTANTS OF *trans*-1,2-DISUBSTITUTED INDANS[a,b]

Compd	R_1	R_2	J_{12} (Hz)	J_{23} (Hz)	J_{24} (Hz)	J_{34} (Hz)	H_1 (Hz)	H_2 (Hz)	H_3 (Hz)	H_4 (Hz)	Other	RMS[n] error	Solvent
12	OH	OH	5.5	7.2	7.0	−15.7	292.3	255.6	189.2	162.0	*g*	0.07	*c*
13	OCH_3	OCH_3	4.6	6.9	5.4	−16.1	278.5	239.5	191.6	160.9	*h*	0.04	*d*
14	$OCOCH_3$	$OCOCH_3$	3.8	7.3	4.8	−16.6	368.6	321.5	205.7	168.8	*i*	0.02	*c*
15	OH	OCHO	4.6				303	313	165	203	*j*		*e*
16	$OCOCH_3$	OCHO	3.9	7.3	4.9	−16.7	371.0	327.4	204.9	168.8	*k*	0.02	*d*
17	OH	Cl	5.5	7.3	6.9	−16.1	305.4	256.8	208.8	179.1	*g*	0.03	*c*
18	OCH_3	Cl	4.1	7.0	5.4	−16.5	281.5	256.3	200.4	173.7	*l*	0.06	*d*
19	$OCOCH_3$	Cl	3.8	6.8	4.7	−16.6	371.4	265.7	209.0	181.8	*m*	0.05	*d*
20	OH	Br	5.4	7.2	6.8	−16.4	313.0	259.2	215.4	188.3	*g*	0.03	*c*
21	Cl	Cl	3.3	6.2	3.8	−16.7	311.5	266.7	204.5	176.1		0.04	*f*
22	Br	Br	1.3	5.0	1.2	−17.5	333.0	282.3	211.5	181.6		0.13	*f*
23	Cl	I	2.9	6.2	3.2	−17.5	326.2	266.8	207.4	182.1		0.05	*f*

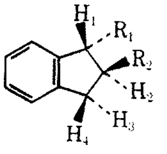
[a] Chemical shifts are in hertz downfield from internal tetramethylsilane at 60 MHz and coupling constants and root mean square error are in hertz. [b] All compounds gave a complex multiplet at 420 to 450 Hz for the aromatic hydrogens. [c] Acetone-d_6. [d] Carbon tetrachloride. [e] DMSO-d_6. [f] Neat liquid. [g] HCl gas added, OH absorption not measured. [h] Methoxy singlets at 203 and 209 Hz. [i] Acetoxy methyl singlets at 115 and 118 Hz. [j] Hydroxyl hydrogen singlet at 342 Hz, aldehyde hydrogen singlet at 497 Hz. [k] Acetoxy methyl singlet at 117 Hz, aldehyde hydrogen singlet at 477 Hz. [l] Methoxy singlet at 204 Hz. [m] Acetoxy methyl at 120 Hz. [n] Root mean square.

were prepared from precursors of known stereochemistry in a stereospecific fashion as described in the Experimental Section. Chlorination of indene in carbon tetrachloride gives both *cis*- and *trans*-1,2-dichloroindans.[7] The stereochemistry of these isomers was proven by determination of their dipole moments, *cis* 2.9 D, *trans* 2.3 D. Addition of bromine to indene in nonpolar solvents produces *cis*- and *trans*-1,2-dibromoindans, but addition of iodine monochloride gives only *trans*-1-chloro-2-iodoindan. The stereochemistry of these last three compounds was deduced by means of nmr spectroscopy using values of vicinal coupling constants (Tables I and II) and the appearance of the signals of the geminal hydrogens at C_3.[5,8]

Nmr Data.—Spectral parameters are listed in Tables I and II; the numbering scheme used is that shown.



cis



trans

Parameters were extracted from the spectra using the LAOCOON II computer program.[9] The hydrogens on the cyclopentene ring exhibited ABMX-type spectra where J_{AX} and J_{BX} are *ca.* 0. In all but compounds **6** and **15** H_1 appeared farthest downfield as a doublet, $J_{12} = 1$–7 Hz, while H_2 gave a sextet or octet at higher field. The geminal pair, H_3 and H_4, appeared at highest field. As noted by Rosen, *et al.*,[5] H_3 and H_4 have very similar chemical shifts in the *cis* isomers and give simple signals of two to four lines. The *trans* isomers have a larger chemical-shift difference and give the expected eight-line pattern with the inner four being most intense. In every case the hydrogen *cis* to the substituent at C_2 (H_4) was assigned at higher field than H_3. The shielding effect of a *cis* substituent on β hydrogens in rigid or semirigid rings has been observed by Wiberg[10] and has been discussed recently by

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(7) C. M. Suter and G. A. Lutz [*J. Amer. Chem. Soc.*, **60**, 1360 (1938)] report the isolation of a single isomer, assumed to be *trans*, after distillation.

(8) Details of the electrophilic additions will be published elsewhere.

(9) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). We would like to thank Professor Bothner-By for sending us a copy of his program.

(10) K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **85**, 2788 (1963).

Andreatta, *et al.*[11, 12] This assignment has the virtue of making J_{23} (*cis*) > J_{24} (*trans*) which is expected for a cyclopentene ring.[1,3-5,14]

Spectral parameters for the *trans* compounds could be determined with good accuracy. All probable errors[15] were less than 0.2 Hz except for dibromide **22**. Since no completely satisfactory set of parameters could be determined for **15**, we report only J_{12} which is determined uniquely by the separation between the lines of the H_1 doublet. In the *cis* compounds the small chemical shift between H_3 and H_4 makes the four outer lines of the H_3H_4 octet too weak to be detected. These simplified spectra do not permit accurate determination of all spectral parameters. A fixed J_{34} value of -16.7 Hz, typical of that observed for the *trans* compounds, was chosen.[16,17] Calculations showed that virtually no changes occurred in the other parameters as J_{34} was varied between -12 and -17 Hz. Probable errors for J_{12} and J_{24} are less than 0.2 Hz except in the few instances noted in Table I. Probable error values for J_{23} are all 0.34 Hz or greater, however.

Owing to the different solubilities of the compounds, spectra were obtained in several different solvents. Although Erickson has observed a large solvent effect on J_{vic} in *dl*-dibromosuccinic anhydride,[1c] normally solvent effects on vicinal H–H coupling constants are small.[18] *trans*-1,2-Dimethoxyindan has a J_{12} of 4.3 Hz in acetone-d_6 and 4.6 Hz in carbon tetrachloride, and J_{12} of *trans*-2-bromo-1-indanol (**20**) changes only 0.2 Hz on changing solvent from acetone-d_6 to pyridine. All samples were *ca.* 12 wt % in the solvent given. Variation of the concentration of **20** in acetone-d_6 from 6 to 21% caused no measurable change in J_{12}.

Electronegativity Corrections.—Karplus has pointed out that vicinal hydrogen coupling constants are functions of four major variables.[16,19] Bond lengths and angles should remain constant in our compounds except for carbonate **5** and acetonide **4**. However, the observed coupling constants will be a function of both dihedral angle[14,18] and effects of electronegative substituents.[13,18,20,21] Sable, *et al.*,[1b] noted that J_{vic} does not vary linearly with substituent electronegativity in tetrasubstituted cyclopentanes and Erickson[1c] observed that J_{trans} actually increases with increasing substituent electronegativity in substituted succinic anhydrides. Both authors attributed the deviation from expected behavior to superposition of conformational and electronegativity effects. Clearly, if they are to give reliable conformational information, our coupling constants must be corrected for electronegativity effects.

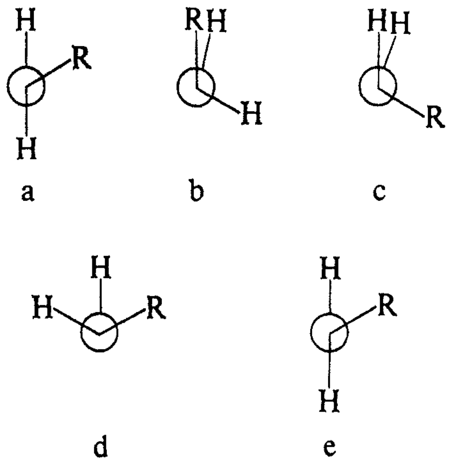

Figure 1.—Conformation of an electronegative substituent (R) and β hydrogen.

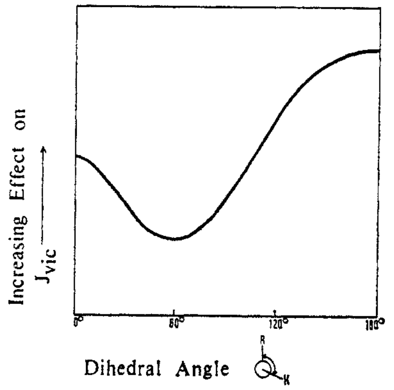

Figure 2.—Conformational dependence of the electronegativity effect on vicinal hydrogen–hydrogen coupling constants.

The diminution of vicinal coupling constants by electronegative substituents in saturated systems is well grounded theoretically[19] and has been verified experimentally.[13,20,21] Theory predicts[19] and experiments show[13,20,22,23] that the effect is conformation dependent. Williams and Bhacca[22] and Booth[23] have shown that the maximum effect obtains when the electronegative substituent is *trans* to the β hydrogen (Figure 1a) and Booth[23] has suggested that a second weaker maximum may exist when the substituent is *cis* to the β hydrogen (Figure 1b). Work on rigid bicyclo[2.2.1]heptenes[20,21] shows that sizable effects are obtained at dihedral angles of 0 (Figure 1b) and 120° (Figure 1c), with that at 120° being the greater. Work of Whitesides, *et al.*,[24] shows negligible effects for an angle of *ca.* 60° (Figures 1d and e). That the effect at 60° is minimal compared to that at 180° is dramatically illustrated by a series of α-halo steroidal ketones[25] in agreement with Williams and Bhacca[24] and Booth.[23] Thus available evidence suggests that the effect decreases with the dihedral angle between the substituent and the β hydrogen in the following order: 180° > 120° > 0° > 60°. This angular dependence is depicted in Figure 2.

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(11) R. H. Andreatta, V. Nair, and A. V. Robertson, *Aust. J. Chem.*, **20**, 2701 (1967).

(12) Additional series of compounds which exhibit this effect are substituted ethylene oxides[13] and 1,1-dichlorocyclopropanes.[13] The carboxyl group does not follow this rule,[10,11] but all of our substituents are considered normal.[11]

(13) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Amer. Chem. Soc.*, **86**, 762 (1964).

(14) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(15) Probable error is defined as the increment in a parameter necessary to double the root mean square error for all parameters.

(16) This is a reasonable value for an indan. *Cf.* A. A. Bothner-By in "Advances in Magnetic Resonance," Vol. I., J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965, p 195.

(17) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, No. 7, 355 (1966).

(18) S. L. Smith and R. H. Cox, *J. Phys. Chem.*, **72**, 198 (1968).

(19) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(20) K. L. Williamson, *ibid.*, **85**, 516 (1963).

(21) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963).

(22) D. H. Williams and N. S. Bhacca, *ibid.*, **86**, 2742 (1964).

(23) H. Booth, *Tetrahedron Lett.*, 411 (1965).

(24) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967).

(25) A. Nikon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *ibid.*, **85**, 2185 (1963).

TABLE III

CORRECTED COUPLING CONSTANTS FOR *cis*-1,2-DISUBSTITUTED INDANS

Compd	R_1	R_2	J^u_{12}, Hz[a]	J^u_{24}, Hz	Sum of van der Waals radii,[b] Å	Electronegativity[c] R_1	R_2
5	Carbonate		11.2	2.6	3.0	3.72	3.72
3	$OCOCH_3$	$OCOCH_3$	9.0	12.0	3.0	3.72	3.72
7	$OCOCH_3$	OCHO	9.0	(9.4)[d]	3.0	3.72	3.72
4	Acetonide		8.2	0.8	3.0	3.31	3.31
9	$OCOCH_3$	Cl	8.0	(7.2)	3.25	3.72	3.25
1	OH	OH	7.9	3.6	3.0	3.43	3.43
6	OH	OCHO	7.9		3.0	3.43	3.72
8	OH	Cl	7.5	(5.6)	3.25	3.43	3.25
2	OCH_3	OCH_3	7.3	11.0	3.0	3.31	3.31
10	Cl	Cl	7.3	(8.2)	3.5	3.25	3.25
11	Br	Br	6.6		3.7	2.96	2.96

[a] The correction calculated by eq 3 was doubled to simulate the effect of the second substituent. The average electronegativity of the two substituents was used in the calculation. [b] Sum of the van der Waals radii for the substituent atoms bonded directly to C_1 and C_2. van der Waals radii from A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964). [c] Values from J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1009 (1961), and ref 21. [d] Less reliable values in parentheses.

TABLE IV

CORRECTED COUPLING CONSTANTS FOR *trans*-1,2-DISUBSTITUTED INDANS

Compd	R_1	R_2	J^u_{12},[a] Hz	J^u_{23}, Hz	J^u_{24}, Hz	Sum of van der Waals radii,[b] Å	Electronegativity[c] R_1	R_2
12	OH	OH	11.9	12.8	12.5	3.0	3.43	3.43
17	OH	Cl	11.2	11.0	11.1	3.25	3.43	3.25
15	OH	OCHO	11.0			3.0	3.43	3.72
16	$OCOCH_3$	OCHO	10.6	15.7	10.5	3.0	3.72	3.72
14	$OCOCH_3$	$OCOCH_3$	10.4	15.7	10.3	3.0	3.72	3.72
20	OH	Br	10.4	10.0	9.5	3.35	3.43	2.96
13	OCH_3	OCH_3	9.2	11.5	9.0	3.0	3.31	3.31
19	$OCOCH_3$	Cl	8.6	11.0	7.6	3.25	3.72	3.25
18	OCH_3	Cl	8.0	11.3	8.7	3.25	3.31	3.25
21	Cl	Cl	6.3	10.0	6.1	3.5	3.25	3.25
23	Cl	I	5.0	7.6	4.0	3.75	3.25	2.66
22	Br	Br	2.0	7.0	1.7	3.7	2.96	2.96

[a] The correction increment calculated with eq 2 was increased by a factor of 1.5 to simulate the effect of the second substituent. The average electronegativity of R_1 and R_2 was used in the calculation. [b] Sum of the van der Waals radii for the substituent atoms bonded directly to C_1 and C_2. van der Waals radii from A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964). [c] Values from J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1009 (1961), and ref 21.

Karplus has derived equations that relate J_{vic} to substituent electronegativity of the form of eq 1 where J is the observed constant, J^u is an unperturbed constant, and ΔX is the electronegativity difference between the substituent and hydrogen.[19] The Karplus value of $m = 0.60$ for *cis* hydrogens (Figure 1c) predicts a much larger effect than that observed in norbornenes.[18,20,21] Use of data of Smith and Cox[18] from 2-substituted hexachloro-5-norbornenes to calculate values for m gives eq 2 and 3 which apply to conformations b and c in Figure 1, respectively. The rigid norbornene molecule is not a perfect model for the more flexible indans. However, we expect that the conformations of the strained cyclopentene ring in indans will not differ grossly from the eclipsed conformation of the model. Thus eq 2 and 3 should apply, at least approximately, to indans. Neglect of the small effect of R_1 and J_{23} and J_{24} should not affect the accuracy of our method significantly.[26]

$$J = J^u(1 - m\Delta X) \quad (1)$$

$$J_{trans} = J^u{}_{trans}(1 - 0.330\Delta X) \quad (2)$$

$$J_{cis} = J_{cis}(1 - 0.157\Delta X) \quad (3)$$

Equations 2 and 3 were used to calculate J^u values. For *cis* compounds (Table III) the calculated correction to J_{12} was doubled to simulate the effect of a second substituent. The average electronegativity of R_1 and R_2 was used in each case. Owing to their large uncertainties, J_{23} values for *cis* compounds were not corrected. Table IV lists J^u values for *trans* compounds. Since J^u should be a function of conformation alone, the two *trans* coupling constants $J^u{}_{12}$ and $J^u{}_{24}$ should be equal for each compound, and the correction to J_{12} was adjusted accordingly. To make $J^u{}_{12} \sim J^u{}_{24}$ for these compounds the correction to J_{12} calculated by eq 2 had to be increased by a factor of 1.5. This suggests that the effects of two electronegative substituents on J_{12} are not additive in this case as we assumed for the *cis* compounds. Fortunately, our conclusions about conformation are not dependent on our assumptions regarding additivity of these effects.

Conformation.—Eclipsing and steric strain will make the planar conformation of indans a high-energy one,[27] and abundant evidence favors nonplanarity of cyclo-

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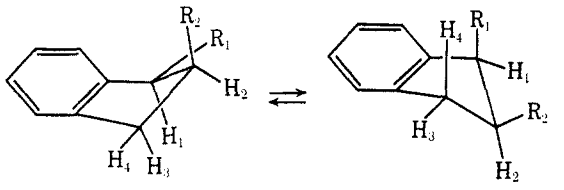
[26] A. D. Cohen and T. Schaffer, *Mol. Phys.*, **10**, 209 (1966).

[27] Calculations and experiment show that *trans*-1,2-dihalocyclopentanes exist as a mixture of diaxial and diequatorial conformers in which the halogen atoms occupy the most puckered part of the ring. *Cf.* (a) C. Altona, H. R. Buys, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **85**, 973,993 (1966); (b) C. Altona, H. R. Buys, H. J. Hageman, and E. Havinga, *Tetrahedron*, **23**, 2265 (1967).

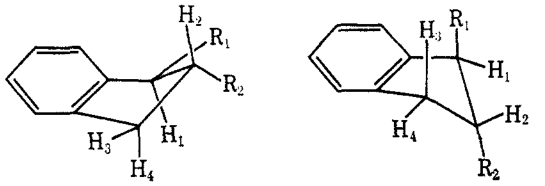
pentenes[2,3] and indans.[4,5] Our data support puckering strongly. For example, many J_{trans} in both series of compounds are too large to be consistent with a planar ring and a dihedral angle of 120°.[14] As for other flexible rings, no linear relationship between vicinal coupling constants and electronegativity is observed. Our data can be interpreted in terms of two puckered conformations shown for *cis* compounds.



cis-ea *cis*-ae

Distortion in either direction from the planar conformation should decrease J^u_{12};[14] so J^u_{12} will decrease as the average degree of puckering increases. The data in Table III reveal that puckering, as measured by J^u_{12}, increases as the combined size of R_1 and R_2, estimated by the sum of van der Waals radii for the atoms directly bonded to C_1 and C_2, increases.[28] However, as the electronegativities of R_1 and R_2 increase causing dipole–dipole repulsions to increase, the compounds become more planar. Clearly, the degree of puckering is controlled by steric rather than by dipole–dipole forces. J^u_{24} is small in the ea conformation but relatively large in the ae conformation.[14] Thus J^u_{24} should be a measure of the relative conformer populations. Scatter among J^u_{24} values in Table III suggests that factors other than R_1–R_2 repulsions control the relative populations. This is reasonable since the R_1–R_2 distance will be equal for the two conformations if they are equally puckered.

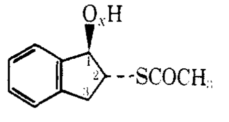
Conformations for *trans*-1,2-disubstituted indans are shown. The two *trans* coupling constants, J^u_{12} and J^u_{24}, should be principally a function of the relative populations of the two conformations as in the *cis* series. The decrease in the size of J^u_{12} and J^u_{24} as the sum of van der Waals radii for R_1 and R_2 increases can be attributed to a depopulation of the ee conformation in which the substituents approach one another closely.[28] As for the *cis* compounds, dipole–dipole repulsions predict the opposite trend. Again, the value of the *cis* coupling constant, J^u_{23}, should decrease with increasing puckering. The observed trend, which requires puckering to increase with substituent size, is reasonable; however some of the J^u_{23} values are unexpectedly large. This is particularly true for **14** and **16**, compounds with very electronegative substituents and J^u_{23} values which include large corrections. These two compounds exist primarily in the ee conformation in which the dihedral angle between R_2 and H_3 <120°. Reference to Figure 2 shows that eq 3, which is for an angle of 120°, should overestimate the electronegativity corrections in these cases.



trans-ee *trans*-aa

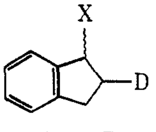
None of the *cis* compounds seems to be far out of place in the substituent size *vs.* degree of pucker correlation. Compounds **8** and **9** should be more puckered relative to **1**, **2**, and **6**, but the coupling constant differences involved are probably too small to be significant. In the *trans* series chlorohydrin **17** and bromohydrin **20** appear to have unusually high ee populations. This may be a characteristic of hydroxy compounds since all compounds bearing a hydroxy group, **12**, **15**, **17**, and **20**, exhibit a marked preference for the ee conformation. It seems unlikely that this preference is caused by intramolecular hydrogen bonding since the more flexible *trans*-1,2-cyclopentanediol exhibits none.[29] Preference for the aa conformation by *trans*-1,2-dihaloindans in particularly striking, and is in agreement with data on *trans*-1,2-dihalocyclohexanes[30] and *trans*-1,2-dihalocyclopentanes.[27] *trans*-1,2-Dibromocyclopentane, for example, is about 80% diaxial conformer at 25° in acetonitrile.[27a]

The stereochemistry of some previously reported indans can be clarified by reference to our data. The 1,3-*cis*-diacetoxy-2-nitroindan of Baer and Achmatowicz[31] is almost certainly the all-*cis* isomer. Because of the high electronegativity of the acetoxy and nitro substituents, the coupling constant values, J_{12} = J_{23} = 5–6 Hz, are consistent only with *cis* stereochemistry. Suitable *trans* model compounds **14**, **16**, and **19** have J_{12} values of 3.8 or 3.9 Hz (Table II) while for the corresponding *cis* derivatives **3**, **7**, and **9**, J_{12} = 5.2–5.4 Hz. Oswald, *et al.*,[32] have reported 1-hydroxy- and 1-peroxy-2-thiolacetates **23** and **24**. The appearance of the signals for the hydrogens at C_3 shows that these are indeed *trans* compounds, though this could hardly have been deduced from the J_{12} values as was reported. Their large J_{12} values suggest that, like the hydroxy compounds reported in this work, they prefer the ee conformation.



23, $x = 1$, $J_{12} = 6$Hz
24, $x = 2$, $J_{12} = 4.5$Hz

The preferred conformation of 1-haloindans can be deduced from data on 1-halo-2-deuterioindans **25** and **26**.[33] Uncorrected coupling constants are, for **25**,



25, X = Br
26, X = Cl

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[28] Measurements made on Dreiding models of planar and *ca.* 25° puckered conformations show that the proposed steric interactions are reasonable.

[29] L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952).

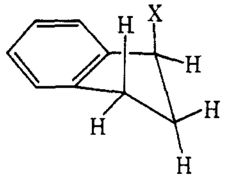
[30] K. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **73**, 717 (1954).

[31] H. H. Baer and B. Achmatowicz, *J. Org. Chem.*, **29**, 3180 (1964).

[32] A. A. Oswald, K. Griesbaum, and W. Naegle, *J. Amer. Chem. Soc.*, **86**, 3791 (1964).

[33] M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245 (1963).

J_{cis} = 7 Hz and J_{trans} = 2.5 Hz; for **26**, J_{cis} = 6 Hz and J_{trans} = 2.5 Hz.[34] Correction for electronegativity effects gives, for **25**, J^u_{cis} = 8 Hz, and J^u_{trans} = 3 Hz; for **26**, J^u_{cis} = 7 Hz and J^u_{trans} = 4 Hz. The small J^u_{trans} values indicate a strong preference for the axial conformation (**27**), and the J^u_{cis} values suggest a moderate degree of puckering (see Tables III and IV).



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In summary, it has been possible, using data on a related rigid system, to correct vicinal coupling constants in indans for the effects of electronegative substituents. The corrected values can be used as the basis of reasonable conformational proposals which are in accord with what is known about conformations of indans and some related systems. A glance at Tables I and II show that our conformational conclusions could not have been reached without such corrections. While qualitatively these corrections are almost certainly correct, their quantitative aspect must still meet the test of independent data.

Experimental Section

Infrared spectra were recorded using Beckman Model IR-5 and IR-10 instruments, and melting points were determined with a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. Preparative vpc was carried out with a Varian-Aerograph A-700 instrument. The Alfred Bernhardt and Schwartzkopf microanalytical laboratories performed the elemental analyses.

Nmr spectra were recorded on Varian Associates A-60 and A-60A instruments using tetramethylsilane as an internal standard. Peak positions were determined on expanded scales by bracketing each group of lines with side bands of the tetramethylsilane signal generated by a Hewlett-Packard 200 CD audio oscillator and calibrated by means of a Hewlett-Packard 5211 B counter. The values used were the average of four determinations, two sweeps in each direction. Spectral parameters were extracted using the LAOCOON II program on a CDC 3600 machine. In appropriate cases several different sets of line assignments were used in part 2 of the program to determine the best set. Coupling constants, except where noted, should be accurate to within ±0.3 Hz; however, chemical shifts were not extrapolated to infinite dilution and should not be regarded as standard values.

Previously Reported 1,2-Disubstituted Indans.—The following compounds are known stereochemistry and were prepared according to descriptions in the reference cited here: **1**,[5] **3**,[35] **4**,[5] **6**,[5] **7**,[5] **8**,[7] **12**,[5] **14**,[36] **15**,[5] **17**,[7] **20**.[37]

cis-**1,2-Dimethoxyindan** (**2**).—A solution of diazomethane (*ca.* 88 mmol) in methylene chloride was prepared by the method of Arndt[38] from 13.2 g (150 mmol) of N-nitroso-N-methylurea and was dried over potassium hydroxide pellets for 1.5 hr. This solution was added over the period of 1 hr to a stirring solution of *cis*-1,2-indandiol[5] (3.3 g, 22 mmol) and boron trifluoride ethyl etherate (0.1 ml, 0.7 mmol) in 200 ml of methylene chloride at 0°. After stirring at 0° for 1 more hr, the reaction mixture was washed with water and saturated aqueous sodium bicarbonate and was dried ($MgSO_4$). Evaporation of the solvent under vacuum left a yellow oil. Distillation at 0.01 mm gave fractions [bp 55–59° (0.9 g), 59–60° (1.0 g), and 60–62° (1.1 g)] for a total yield of 80%. Treatment of the middle fraction with Norit in hot acetone, removal of the solvent, and evaporative distillation at 40° (0.01 mm) gave a colorless oil which was analytically pure: ir (neat, cm^{-1}) 1600, 1460 (aromatic C=C), 1125, 1085 (C—O), 750 (*o*-phenylene).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.24; H, 7.98.

trans-**1,2-Dimethoxyindan** (**13**).—A dry solution of diazomethane (*ca.* 9.4 mmol) in 200 ml of methylene chloride[38] was added dropwise during 1 hr to a stirring solution of *trans*-1,2-indandiol[5] (0.7 g, 4.7 mmol) and boron trifluoride ethyl etherate (0.3 ml, 1.7 mmol) in 200 ml of dry ethyl acetate held at 5°. After 1 more hour of stirring at 5°, the reaction mixture was washed with saturated aqueous sodium bicarbonate, and was dried ($MgSO_4$). Evaporation of the solvent under vacuum left a yellow oil that was evaporatively distilled at 45° (0.01 mm) to give 0.1 g (9%) of a clear oil. Preparative vpc on a $^3/_8$ in. × 10 ft 25% DC 200 silicone oil on Chromosorb W gave material of analytical purity: ir (CCl_4, cm^{-1}) 1460 (aromatic C=C), 1095 (C—O).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.82; H, 7.92.

trans-**2-Chloro-1-methoxyindan** (**18**).—A dry solution of diazomethane (*ca.* 33 mmol) in 100 ml of methylene chloride[38] was added during 0.5 hr to a stirring solution of *trans*-2-chloro-1-indanol[7] (5.0 g, 30 mmol) and boron trifluoride ethyl etherate (1.0 ml, 7 mmol) in 300 ml of dry methylene chloride at 0°. After stirring for 1 more hr at 0°, the reaction mixture was washed with water, saturated aqueous sodium bicarbonate, and again with water, and was dried ($MgSO_4$). Removal of the solvent under vacuum and evaporative distillation at 40° (0.01 mm) gave 1.0 g (18%) of a slightly yellow oil. Treatment with Norit in hot acetone, removal of the solvent, and evaporative distillation at 40° (0.01 mm) gave a clear analytically pure oil: ir (neat, cm^{-1}) 1610, 1480 (aromatic C=C), 1085 (C—O), 740 (*o*-phenylene).

Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.76; H, 6.07; Cl, 19.41. Found: C, 65.65; H, 6.21; Cl, 19.27.

cis-**1-Acetoxy-2-chloroindan** (**9**).—Acetyl chloride (3.0 ml, 43 mmol) was added dropwise to a stirring solution of *cis*-2-chloro-1-indanol[7] (1.1 g, 6.6 mmol) in 15 ml of dry pyridine at 0°. The reaction flask was stoppered, and stirring was continued at 0° for 1 hr. The reaction mixture was poured into 100 ml of benzene, and was washed consecutively with water, dilute hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water. Drying ($MgSO_4$) and evaporation of the solvent under vacuum left a red oil. Evaporative distillation at 70° (0.02 mm) gave 0.8 g (85%) of **9** as a light red oil. Treatment with Norit in hot acetone and evaporative distillation gave a colorless analytical sample: ir (neat, cm^{-1}) 1740 (C=O), 1230 (acetate C—O), 1060 (ether C—O), 740 (*o*-phenylene).

Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.71; H, 5.26; Cl, 16.83. Found: C, 62.60; H, 5.72; Cl, 16.73.

trans-**1-Acetoxy-2-chloroindan** (**19**).—Acetyl chloride (5.0 ml, 70 mmol) was added dropwise to a stirring solution of *trans*-2-chloro-1-indanol[7] (40 g, 24 mmol) in 30 ml of dry pyridine at 0°. The reaction flask was stoppered, and stirring was continued at 0° for 1 hr. The reaction mixture was taken up in 250 ml of benzene, and the benzene solution was washed consecutively with water, dilute hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water. Drying ($MgSO_4$) and removal of benzene under vacuum gave a red oil that afforded 1.6 g (35%) of **19** as a yellow oil on evaporative distillation at 83° (0.02 mm). Treatment with Norit in hot acetone followed by evaporative distillation at 50° (0.01 mm) afforded an analytically pure colorless oil: ir (neat, cm^{-1}) 1740 (C=O), 1225 (acetate C—O), 1040 (ether C—O), 745 (*o*-phenylene).

Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.71; H, 5.26; Cl, 16.83. Found: C, 62.30; H, 5.48; Cl, 16.68.

trans-**1-Acetoxy-2-formyloxyindan** (**16**).—Acetyl chloride (1.5 ml, 20 mmol) was added slowly to a stirring solution of *trans*-2-formyloxy-1-indanol[5] in 15 ml of dry pyridine at 0°, and stirring was continued for 1 hr at room temperature. A solution of the reaction mixture in 75 ml of benzene was washed consecutively with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water. Drying ($MgSO_4$) and removal of the

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(34) Values from measurements on spectra in ref 33.

(35) P. W. Verkade, J. Coops, A. Verkade-Sandbergen, and C. J. Mann, *Ann. Chem.*, **477**, 280 (1930).

(36) W. F. Whitmore and A. I. Gebhart, *J. Amer. Chem. Soc.*, **64**, 912 (1942).

(37) C. M. Suter and H. B. Milne, *ibid.*, **62**, 3473 (1940).

(38) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 165.

solvent under vacuum gave a yellow oil that was treated with Norit in hot acetone to give **16** as a clear oil, 0.22 g (50%). Preparative vpc on a $^3/_8$ in. × 10 ft 25% DC 200 silicone oil on chromosorb W column gave material of analytical purity: ir (neat, cm^{-1}) 1745–1735 broad (C=O), 1230 (acetate C—O), 1160 (formate C—O), 740 (*o*-phenylene).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.59; H, 5.38.

cis-**1,2-Indandiol Carbonate** (**5**).—A flask containing *cis*-1,2-indandiol[5] (1.6 g, 10.6 mmol) and 10 ml of pyridine in 250 ml of ether was placed in an efficient fume hood and cooled in an ice bath. Phosgene was bubbled slowly into the solution for 1 hr, and the reaction mixture was stirred for an additional 12 hr. Excess phosgene and *ca.* two-thirds of the ether were removed under reduced pressure in the fume hood. The resulting slurry was washed with saturated aqueous sodium bicarbonate, 3 *N* hydrochloric acid, and again with the bicarbonate solution. A white solid formed upon removal of the solvent. Recrystallization from ether gave 0.26 g (14%) of **5** as a white solid: mp 74–75°; ir (Nujol, cm^{-1}) 1790 (C=O), 1060 and 1170 (C—O), 750 (*o*-phenylene).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 67.92; H, 4.67.

Preparation and Dipole Moments and *cis*- (**10**) **and** *trans*-**1,2-Dichloroindan** (**21**).—A solution of indene[39] (1.0 g, 8.6 mmol) in 25 ml of carbon tetrachloride was cooled in an ice bath and stirred as chlorine was added through a glass frit until its yellow color persisted. Excess chlorine was destroyed by washing the reaction mixture with several portions of saturated aqueous sodium thiosulfate. The solution was dried ($MgSO_4$), and the solvent was evaporated under vacuum to give a mixture of *cis*- and *trans*-1,2-dichloroindans. In benzene solution the H_1 nmr doublets of these isomers were well resolved, and careful integration of the nmr signals showed that the composition of this crude sample was 30% *cis* (J_{12} = 5.1 Hz) and 70% *trans* (J_{12} = 3.3 Hz). Temperatures necessary for vacuum distillation and vpc work caused loss of hydrogen chloride from and decomposition of the crude dichlorides. Column chromatography on Florisil with petroleum ether (bp 50–60°) as eluent gave initial fractions that contained only the *trans* isomer, n^{25}D 1.5675. Though it was impossible to obtain pure *cis* isomer by this method, later fractions were enriched in this isomer and were suitable for subsequent work.

Dipole moments were determined in benzene by the method described by Shoemaker and Garland[40] using a Sargent oscillometer, Model V. Pure *trans* was used but the *cis* sample was 66 mol % *cis* and 34 mol % *trans*. Dipole moments were calculated as *trans* 2.3 ± 0.2 D and "*cis*" 2.7 ± 0.2 D. Use of the equation $\mu^2 = N_1\mu_1^2 + N_2\mu_2^2$ gave a value of 2.9 ± 0.2 D for pure *cis* isomer.

cis- **and** *trans*-**1,2-Dibromoindans 11 and 22**.—Bromine was added dropwise to a stirring solution of indene[39] (5.0 g) in 25 ml of dry ethyl ether at 0–5° until a red color persisted. The reaction mixture was washed with saturated aqueous sodium thiosulfate and was dried ($MgSO_4$). Evaporation of the solvent under vacuum left a crude oil which was determined to be 80–90% *trans* isomer by integration of the H_1 nmr signals of a neat sample. The value of J_{12} = 5.0 Hz for the *cis* isomer was obtained by measuring the separation of the H_1 doublet in these spectra. Low-temperature crystallization from petroleum ether as described by Winstein and Roberts[41] afforded pure *trans*-1,2-dibromoindan (**22**).

trans-**1-Chloro-2-iodoindan** (**23**).—Iodine chloride was added slowly to a solution of indene[39] (5.0 g, 43 mmol) in 25 ml of carbon tetrachloride cooled in an ice–salt bath. Addition was regulated to keep the temperature of the reaction mixture below 0° and was discontinued when further addition caused no rise in temperature. The reaction mixture was washed with aqueous sodium thiosulfate and was dried ($MgSO_4$). Evaporation of the solvent under vacuum left a pink oil that rapidly became dark and could not be stored without decomposition even under refrigeration: ir (neat, cm^{-1}) 1610 and 1475 (aromatic C=C), 800–700 (C-Cl and *o*-phenylene). Nmr spectroscopy shows that the product is contaminated by *ca.* 10% *cis*-1,2-dichloroindan.

Registry No.—**1**, 4647-42-1; **2**, 19597-95-6; **3**, 19597-96-7; **4**, 19597-97-8; **5**, 19597-98-9; **6**, 19597-99-0; **7**, 19598-00-6; **8**, 19598-01-7; **9**, 19598-02-8; **10**, 19598-03-9; **11**, 19598-04-0; **12**, 4647-43-2; **13**, 19598-06-2; **14**, 19598-07-3; **15**, 19598-08-4; **16**, 19598-09-5; **17**, 19598-10-8; **18**, 19598-11-9; **19**, 19598-12-0; **20**, 10368-44-2; **21**, 19598-14-2; **22**, 19598-15-3; **23**, 19598-16-4.

Acknowledgment.—We wish to acknowledge grants from the University of Massachusetts Research Council and Research Computing Center in support of this work.

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[39] 97.5% stabilized with 90 ppm of *p*-toluhydroquinone, Neville Chemical Co., Neville Island, Pa.

[40] D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 275.

[41] S. Winstein and R. M. Roberts, *J. Amer. Chem. Soc.*, **75**, 2297 (1953).

dibromoindan (22).