Regioselectivity in the Reductive Cleavage of *syn*- and *anti*-2-Methylspiro[cyclopropane-1,1′-indene]. Elucidation of the Role of Steric Effects

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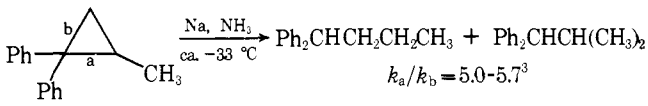
Abstract: The title compounds (**11** and **12**, respectively) have been shown to suffer reductive cleavage at essentially the same rate on treatment with lithium or sodium in liquid ammonia at ca. −33 °C. Six cyclopropyl ring-opened products have been identified as products of this reaction. The regioselectivity [opening of bond a relative to bond b (k_a/k_b)] is 4 for **11** and 0.6 for **12** (in lithium–liquid ammonia). These opposite regioselectivites are explained in part by the much larger steric interaction between the methyl group and the adjacent peri hydrogen in **11** relative to that between the methyl group and the adjacent five-membered ring hydrogen in **12** during cleavage of bond b. All currently available data are consistent with the expectation that substitution of a methyl group on a bond undergoing cleavage will cause a *retardation* of the rate of cleavage in the absence of major steric effects.

The study of regioselectivity in reductive cleavages of cyclopropyl rings conjugated with π-electron systems is of interest both because of the potential synthetic utility of this class of reactions and because of the variety of different factors which can influence the direction of cleavage.[1] In this study we are concerned with the effect of methyl groups on the course of these reactions.

Walborsky and co-workers[2,3] have reported that the regioselectivities (which we have defined as k_a/k_b, where bond a is the more substituted cyclopropyl bond of the two which are cleaved)[1,4] in **1** and **2** are in favor of opening of bond a by a



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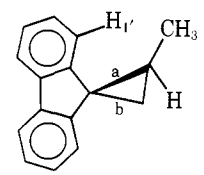

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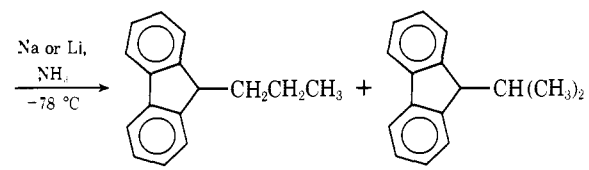
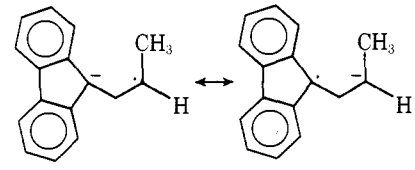
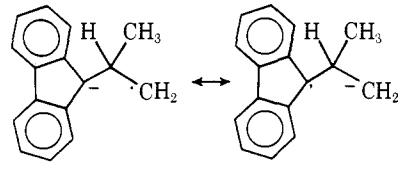


significant factor. These authors argued that since steric interaction between the methyl group and the aromatic ring in **2** is considerably less than in **1** due to the rigidity and planarity of the fluorenyl moiety, steric effects are less important than electronic considerations. It was therefore concluded that the direction of cleavage is determined by the stability of the two anion radicals **3** and **4** (i.e., of the transition states leading to them) which were assumed to be intermediates in the reduction. Since **3** and **4** have more of the negative charge on the fluorenyl moiety (resonance forms **3a** and **4a** were assumed to be the major contributors) and since **3a** is a secondary radical whereas **4a** is a primary radical, it was argued that cleavage of bond a (to afford radical anion **3**) should be favored.[3] Bellamy and co-workers have recently employed similar reasoning on using regioselectivity as a criterion for charge distribution in the transition state for the reductive cleavage of *trans*-1-acetyl-2-methylcyclopropane.[6]

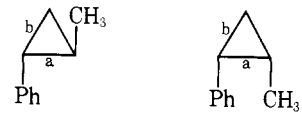


3a **3**

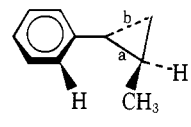


4a **4**

We have previously reported that **5** and **6** exhibit large regioselectivities in opposite directions on reductive cleavage with lithium in liquid ammonia.[1,4] The preference for bond b cleavage in **5** was rationalized on the basis of a destabilizing effect of the methyl group on cleavage of bond a. This destabilization could be due to any of a number of electronic effects due to the methyl group, including an inductive effect and steric hindrance to solvation or to ion pairing. The inverse regioselectivity in **6** was attributed to a destabilization of the transition state for bond b cleavage (**7**) due to interaction between an ortho hydrogen and the methyl group in the conformation which allows maximum overlap between the π orbitals of the phenyl ring and the incipient benzylic p orbital.[4,7]



	5	**6**
k_a/k_b(−33 °C)	0.005	61
k_a/k_b(25 °C)	0.017	20.5



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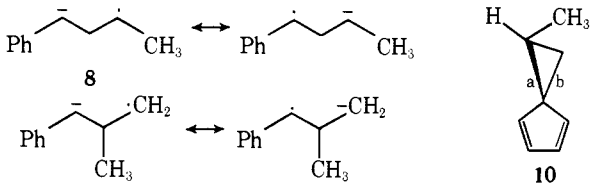
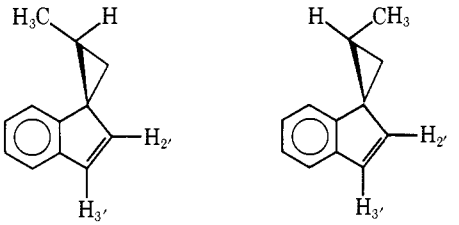
Our view that methyl exerts a rate-retarding effect when substituted on a bond undergoing cleavage is supported by kinetic studies which show that the activation energies for cleavage of bond a in **5** and **6** are greater by 2.5 and 2.3 kcal/mol, respectively, than is that for phenylcyclopropane after correction for ground-state strain in **5** and **6** and for the statistical factor of 2 in phenylcyclopropane. It would therefore be of considerable interest if methyl were shown to exert a rate-enhancing effect in **2.** It is conceivable that opposite effects of methyl might obtain in **2** and **5** if resonance forms **3a** and **4a** were significantly more important than the equivalent contributing structures in the cleavage of **5** (**8** and **9,** respectively). A priori this is not unreasonable in view of the much greater pK_a of toluene relative to fluorene,[8] but we did not feel that this rationale would withstand closer scrutiny since the methyl group also has a rate-retarding influence on bond a cleavage in **10** (in lithium in liquid ammonia) even though the pK_a of cyclopentadiene is much lower than that of fluorene.[8]

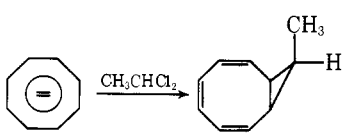


In our view, the regioselectivity in **2** is primarily determined by a destabilizing methyl peri hydrogen ($H_{1'}$ in **2**) interaction during cleavage of bond b and not by an electronic effect of methyl.[1] A study of the cleavage of **11** and **12** provides a nearly ideal test of this question since the electronic effect of methyl will be essentially identical in these two isomers, whereas intramolecular steric effects will differ significantly. Note that the cleavages of **11** and **12** are akin to those of **2** and **10,** respectively, from a steric standpoint. In this paper we report the results of our investigations of the reductive cleavages of **11** and **12** which clearly demonstrate that the regioselectivities in **2** and **11** are dominated by steric interactions, whereas those in **10** and **12** are controlled by a destabilizing methyl electronic effect.



Results

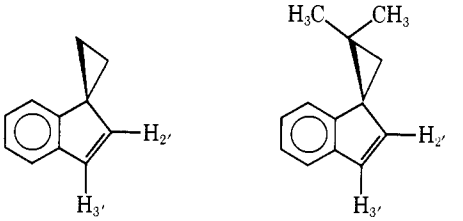
A 63:37 mixture of **11** and **12,** respectively, was prepared in 60% yield by the treatment of indene with sodium in liquid ammonia, followed by the addition of 1,2-dibromopropane.[9] The regioselectivity observed in this synthesis is interesting and may be related to the essentially exclusive formation of syn isomer **13** on treatment of the cyclooctatetraene dianion with 1,1-dichloroethane.[10]



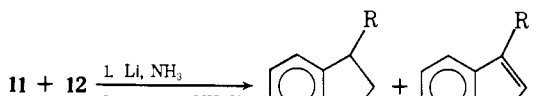
We were not able to even partially separate **11** and **12** on any of about eight gas chromatography columns which were investigated. However, these isomers could be separated with great difficulty by high-pressure liquid chromatography (HPLC). This separation, which was the key to the solving of this problem, was accomplished with an efficiency of ca. 1000 theoretical plates and a resolution of ca. 1.0 by eluting on coupled octadecylsilyl (ODS) preparative columns with 40% methanol/60% water at 70 °C.[11] Fractions of >97% purity could be obtained by discarding the fraction in the valley between the two compounds. Slightly better separations could be achieved in a much shorter time with a newer Zorbax ODS column.

The major difference in the NMR spectra of these two compounds lies in the upfield doublets of the AB quartets of the olefinic protons. These appear at δ 5.98 and 6.28 in the first and second eluting isomers, respectively, and were assigned to $H_{2'}$ since the cyclopropyl ring is expected to exert a net shielding effect relative to the benzo ring adjacent to $H_{3'}$.[12]

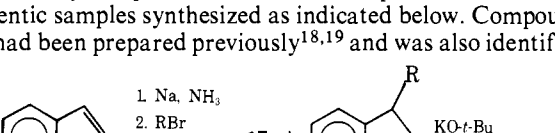
The assignment of the exact structures was made by comparison of the above data with the corresponding NMR data for **14** and **15.** The former compound was available from another study,[13] whereas the latter was prepared by the photolysis of diazoindene[14] in the presence of excess isobutylene.[15] The doublet for $H_{2'}$ appears at δ 6.03 and 6.31 in **14** and **15,** respectively. This indicates that **11** and **12** are the first and second eluting isomers, respectively, since the methyl group syn to $H_{2'}$ is expected to have the greatest influence on the chemical shift of that proton.



When a 63:37 mixture of **11** and **12** was treated with a tenfold equivalent excess of lithium in liquid ammonia at ca. −33 °C for 1 h, followed by quenching with aqueous ammonium chloride, a complex mixture of at least six compounds (32% **16a,** 55% **16b,** 4% **16c,** 2% **17a,** 6% **17b,** and 1% **17c**) was obtained. Compounds **16a,**[16] **16b, 17a,**[17] **17b,**[18] and **17c**[19] were identified by comparison of their NMR spectra with those of authentic samples synthesized as indicated below. Compound **16c** had been prepared previously[18,19] and was also identified



a, R = *i*-Pr
b, R = *n*-Pr
c, R = allyl



(major product)

a, R = *i*-Pr
b, R = *n*-Pr
c, R = allyl

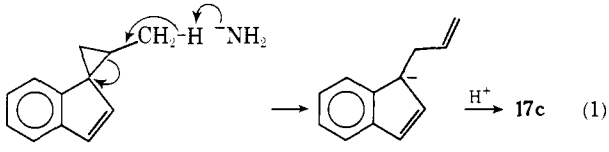
17 + 18 $\xrightarrow{H_2, Pt}$ 16

a, R = *i*-Pr
b, R = *n*-Pr

on the basis of its NMR spectrum.[20] Since many of these products, as well as intermediates **18a**,[21] **18b**,[21b] and **18c**,[19] have been incompletely characterized in the literature, we have listed full infrared and NMR spectral data in the Experimental Section.

Reductive cleavage of **11** and **12** with sodium in liquid ammonia for 10 min under otherwise identical conditions gave similar results except that the product mixture (37% **16a**, 56% **16b**, 2% **16c**, 1% **17a**, 3% **17b**, and 0% **17c**) reflected a slightly higher degree of reduction. When the lithium reaction mixture was quenched with ethanol instead of aqueous ammonium chloride, two additional products with GLC retention times shorter than those of any of the other products were obtained. These were not investigated further but presumably arise from benzo ring reduction.

Control experiments have established that the material balance in these reactions is high (>90%), that **17a** is reduced to **16a**, and that **17c**[22] is reduced to **16b** and **16c** under the reaction conditions (with either lithium or sodium). (The latter result is in accord with the expectation that an indenyl double bond will suffer reduction faster than an allylic double bond.) Furthermore, no more than 15% of a 2:1 mixture of **11** and **12** is converted to **17c** when treated with a tenfold excess of sodium amide in liquid ammonia for 1 h at −33 °C, and no reaction at all occurs with lithium amide. This excludes the possibility that **17c** is formed by reaction of **11** and **12** with amide ion produced on reductive cleavage (eq 1).

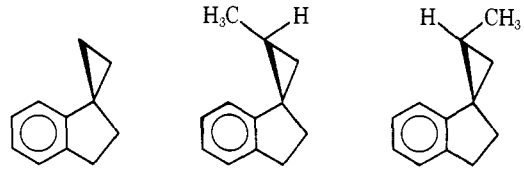


(1)

A 63:37 mixture of **11** and **12** which had been subjected to reductive cleavage conditions with lithium and sodium (90 and 85% loss of starting material, respectively) afforded an isomeric distribution of recovered starting material essentially identical within experimental error (65:35) with the original composition. Both isomers were shown to be completely soluble under these conditions. Furthermore, both **11** and **12** (≥97% pure) showed essentially the same isomeric purity both before and after reductive cleavage. These experiments demonstrate that the two isomers have approximately the same rates of ring opening and that epimerization does not precede cleavage.

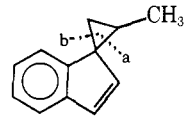
In order to establish that reaction of **11** or **12** with lithium results initially in cyclopropyl ring cleavage rather than in reduction of the indenyl double bond, the rate of reaction of a 63:37 mixture of **11** and **12** was compared with that of **19**[23] (which was prepared by the catalytic reduction of **14**). By analogy to the greater rate for reductive cleavage of phenylcyclopropane compared with its methyl-substituted derivatives,[1,24] the rate of cleavage of **19** should be greater than that of **20** or **21**, if the latter are formed by an initial reduction of the indenyl double bonds of **11** or **12**, respectively. Under the reaction conditions (10-fold equivalent excess sodium in ammonia at −33 °C), both **19** and the mixture of **11** and **12** exhibited pseudo-first-order reaction rate profiles, with **11** and **12** disappearing about 20 times faster than **19**. Since **20** and **21** were not observed in the reaction mixture under conditions where their slower reaction rates would dictate their accumulation, the composition of product mixtures obtained in the reaction of **11** and **12** must be determined by the regioselectivity of the initial opening of the cyclopropyl ring of these isomers.

The reductive cleavages of essentially pure **11** and **12** gave the product mixtures listed in Table I. The regioselectivities (k_a/k_b) were calculated from these data to be 4 and 0.6 for **11** and **12**, respectively. Finally, the fact that **11** and **12** suffer



19 **20** **21**

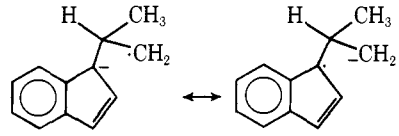
reductive cleavage ($k_a + k_b$) at essentially the same rate, combined with the values of k_a/k_b for each compound, allows one to calculate the following relative rates: $k_a(\mathbf{11})/k_a(\mathbf{12}) = 2$ and $k_b(\mathbf{11})/k_b(\mathbf{12}) = 0.3$.



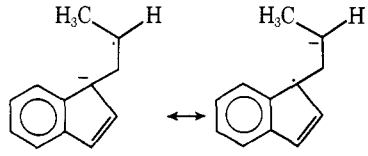
11 or **12**

Discussion

The observed regioselectivities are in accord with our previous prediction.[1] If no steric effects contribute to the stabilities of the transition states leading to radical anions **22** and **23**, as



22



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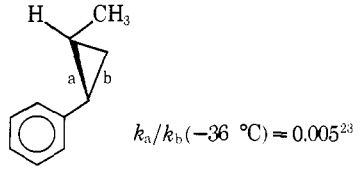
previously suggested for the cleavages of **1** and **2**,[2,3] then essentially identical regioselectivities should be observed for **11** and **12**. The value of k_a/k_b for **11** is about seven times greater than that for **12**, but the important point is that the regioselectivities occur in *opposite* directions. The following discussion will suggest that this provides strong evidence that steric effects play a significant role in the reactivity of at least one of these isomers.

Electronic Effects. The role of electronic effects is best exemplified by the low value of k_a/k_b in **5**.[4,24] There are no major



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steric effects in the cleavage of this compound since the methyl and phenyl groups are trans to each other. This result, therefore, suggests that a methyl group exerts a rate-retarding electronic effect when substituted on the carbon of a bond undergoing reductive cleavage.

It is well known that alkyl groups substituted at negatively charged sites in compounds in solution display a destabilizing influence relative to the corresponding unsubstituted compounds, although examples of a small effect in the opposite direction are known.[25] Various suggestions have been made to explain this behavior, including destabilizing inductive effects,[26,27] unspecified steric factors,[28] and steric hindrance to contact ion pairing[29] or to solvation in contact ion pairing.[26] It has been argued that the inductive effect (σ_I) of alkyl groups

Table I. Product Distributions for the Reductive Cleavage of 0.015 M **11** or **12** in 0.3 N Lithium in Liquid Ammonia[a]

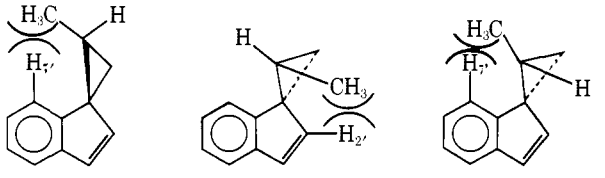
Product	Bond cleaved	Relative yield (%) starting from: **11**	**11**	**11**	**11**[b,c]	**12**	**12**	**12**[b]
16a	b	18.8	15.5	19.9	18.9	57.6	52.1	66.8
16b	a	69.0	64.4	63.7	72.0	29.6	37.0	29.3
16c	a	4.4	2.6	2.6	2.4	3.2	0.3	0.9
17a	b	1.3	2.2	2.5	0.4	5.7	9.3	2.3
17b	a	5.3	7.5	7.8	4.4	1.5	0.8	0.6
17c	a	1.0	0.8	2.9		2.2	2.0	
	k_a/k_b	4.0	4.3	3.4	4.1	0.58	0.65	0.45

[a] For 1 h at −33 °C; quenched with saturated aqueous ammonium chloride. [b] Reduction with sodium. [c] There was also 1.9% of an unknown component with a retention time shorter than that of **16a.**

is essentially equal to that of hydrogen,[30] except perhaps when the substituent is attached to an sp^2 carbon,[25-27] in which case alkyl groups might be slightly destabilizing. We have attributed the regioselectivity in compounds where $k_a/k_b < 1$ primarily to a destabilizing methyl electronic effect which probably includes one or more of the effects discussed above.

Steric Effects. Steric effects may be operative in ground or transition states. Since the products from both bond a and bond b cleavage in a given compound all originate from the same ground state, only effects in the transition states need to be considered in evaluating k_a/k_b. On the other hand, ground-state effects must also be considered when comparing rates in different compounds. An examination of molecular models indicates that there may be at least three interactions of the methyl group which influence the rates of ring opening in **11** and **12.** First of all, there is an interaction between the methyl group and $H_{7'}$ in **11,** the relief of which probably accounts for the greater rate of bond a opening in **11** compared with that in **12.** We term this an a(1,4) interaction because it promotes the opening of bond a and occurs in the ground state between a methyl and a hydrogen which are disposed 1,4 to each other.

The other two steric effects involve interactions between the methyl group and a proximate hydrogen during cleavage of bond b. As ring opening occurs, the developing isopropyl group moves into the plane of the adjacent five-membered ring and an increased methyl-$H_{2'}$ or methyl-$H_{7'}$ interaction results. These are termed b(1,3)‡ and b(1,4)‡ interactions, respectively, because they occur in the transition state for opening of bond b.

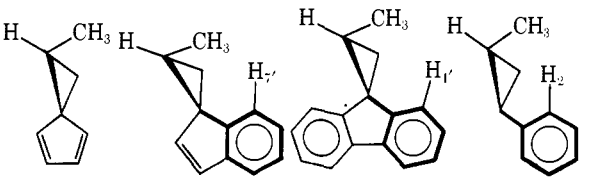


a(1,4) interaction b(1,3)‡ interaction b(1,4)‡ interaction

The various relative rates can now be rationalized as follows: (a) k_a(**11**) > k_b(**11**) because the b(1,4)‡ interaction > the methyl electronic effect retarding opening of bond a; (b) k_b(**12**) > k_a(**12**) because the methyl electronic effect on bond a cleavage > the b(1,3)‡ interaction; (c) k_a(**11**) > k_a(**12**) because of the a(1,4) interaction in **11;** and (d) k_b(**12**) > k_b(**11**) because the b(1,4)‡ interaction in **11** > the b(1,3)‡ interaction in **12** and the a(1,4) interaction in **11.**

Effect of Transition State Structure on Regioselectivity. The comparison of regioselectivities in different compounds is quite complex, not only because of the different steric effects involved, but also because the several transition states will have different charge distributions and degrees of bond breaking. These in turn cause significant variations in the magnitude of the steric and electronic effects caused by methyl substitution.

Series I



	10	**11**	**2**	**6**
k_a/k_b (−33 °C)	0.2	4	13(est)	61

This factor is probably not very important when comparing **11** and **12,** but it is probably quite important when comparing the reactivity of the compounds in Series I. These are listed in order of increasing regioselectivity for cleavage with lithium in liquid ammonia at ca. −33 °C and encompass a range of *over two orders of magnitude.*

It is unlikely that the large increase in regioselectivity observed on going from **5** to **10** (a factor of 40) is due solely to the relatively small b(1,3)‡ interaction in **10.** We suggest that because of the much greater reactivity of **10** (cleavage occurs instantaneously at −33 °C) compared with **5** ($t_{1/2}$ (−33 °C) > 1 day),[24] there is less bond breaking and less negative charge on the methyl-substituted carbon in the transition state for opening of bond a in **10.** This point is in accord with molecular orbital calculations and with the much greater acidity of cyclopentadiene relative to toluene.[8] We therefore anticipate that the methyl electronic effect which retards cleavage of bond a will increase from left to right in Series I.

However, the regioselectivities in Series I also increase in the same order. This can best be explained by the previously discussed steric effects which serve to shift the regioselectivity in the direction opposite to that caused by the electronic effect. The increase in k_a/k_b between **10** and **11** is not unexpected for the same reasons that we used to explain the smaller regioselectivity of **12** compared with **11** (vide supra). However, the further increase in k_a/k_b on going from **11** to **2** and **6** is less obvious. All three compounds are *cis*-2-methylphenylcyclopropanes (see darker bonds in Series I) and therefore all experience b(1,4)‡ interactions on opening of bond b. (Structure **7** illustrates this interaction in **6.**) Furthermore, **6** has a reduced a(1,4) interaction because of its conformational mobility in the ground state and yet still has the largest regioselectivity in Series I.

This behavior can be explained on the basis of increased b(1,4)‡ interaction in the order **11** < **2** < **6** due to increased bond breaking in the transition states. This is consistent with the increase in pK_a in the order indene < fluorene < toluene[8] and with the much greater reactivity of **11** ($t_{1/2}$ (−33 °C) ≈ 12 min) compared with **6** ($t_{1/2}$ (−33 °C) > 1 day).[24] Further evidence for a change in transition-state geometry is provided by the threefold increase in regioselectivity between **10** and **12.**

Both experience b(1,3)‡ interactions, but that in **12** is probably larger due to increased bond breaking in the transition state. Once again, this is consistent with the greater reactivity of **10** and with the relative pK_a values of cyclopentadiene and indene.

Summary and Conclusions

On the basis of the present evidence, we conclude that the large values of k_a/k_b found for **1**[2] and **2**[3] are primarily the result of steric hindrance during bond b cleavage. The data can be rationalized on the basis of several different types of steric effects and both ground and transition states are affected. Finally, all current evidence suggests that a methyl substituent on a cyclopropyl bond undergoing cleavage exerts a destabilizing electronic effect which retards the rate of cleavage of that bond. In principle it might be possible to distinguish between monoanionic and dianionic transition states on the basis of the effect of methyl groups on regioselectivity,[5] but more information than is currently available is required.

Experimental Section

Infrared (ir) spectra were recorded on a Perkin-Elmer Model 337 grating spectrometer and were obtained on solutions in 0.1-mm NaCl cells or on neat samples in a 0.025-mm KBr cell. Only major, distinguishing bands are given. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60-D spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Preparative GLC separations were performed on a Varian-Aerograph A-90P3 thermal conductivity instrument equipped with 0.25 in. copper columns. Analytical GLC separations were conducted on a Varian Aerograph Series 1200 flame-ionization gas chromatograph equipped with 0.125 in. columns. Peak areas were determined with a Hewlett-Packard 3370-A integrator. The following columns were used in GLC separations: A, 20% TCEP on 100/120 mesh Chromosorb P, 1 ft × 0.25 in.; B, 20% Igepal CO 880 on Chromosorb P, 2 ft × 0.25 in.; C, 20% Carbowax 20M on 100/120 mesh Chromosorb P, 3 ft × 0.25 in.; D, 20% Carbowax 20M on 80/100 mesh Diatoport S, 1.5 m × 0.125 in.; E, 10% Carbowax 20M on 70/80 mesh Chromosorb P, 10 ft × 0.25 in.; F, 7% Igepal CO 880 on 80/100 mesh Chromosorb P, 7 ft × 0.125 in.; G, 20% Carbowax 20M on 80/100 mesh Chromosorb P, 1.5 m × 0.25 in. Liquid–liquid chromatography was performed on a du Pont Model 830 liquid chromatograph. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer. Microanalyses were performed by Dr. Franz Kasler of the University of Maryland, Department of Chemistry.

***syn*- and *anti*-2-Methylspiro[cyclopropane-1,1′-indene] (11 and 12).** Distilled indene (41.6 g, 0.36 mol) was slowly added to a solution of 4.84 g (0.21 g-atom) of sodium in 300 ml of liquid ammonia in a dry ice–acetone bath. The reaction mixture was then treated dropwise with 23.4 g (0.21 mol) of 1,2-dibromopropane. After stirring for 2 h, pentane was added, and the reaction was quenched with saturated aqueous NH_4Cl (60 ml). After the ammonia had evaporated, the reaction mixture was diluted with water (250 ml), the layers were separated, the aqueous layer was washed with 200 ml of pentane, and the combined organic solutions were washed with 150 ml of H_2O. The solvent was then removed by rotary evaporation, and the residue was distilled [64–70 °C (0.07 mm)] to afford 13.1 g (66%) of **11** and **12.** Analysis by NMR spectroscopy indicated a 63:37 mixture of the syn and anti isomers, respectively. These were separated (see Results section) on two coupled 1 in. × 2 ft du Pont octadecylsilyl (ODS) liquid chromatography columns (40% MeOH/H_2O, 60 °C, 1000 psi). Final purification was effected by passing each isomer through GLC column A at 90 °C. **11:** ir (neat) 1380, 1355, 1280, 1129, 1045, 875, 865, and 660 cm^{-1}; NMR (CCl_4) δ 7.4–6.9 (m, 4 H, benzo), 6.75 (d, $H_{3'}$, $J_{2'3'}$ = 5.5 Hz), 5.98 (d, $H_{2'}$, $J_{2'3'}$ = 5.5 Hz), 2.0–1.4 (m, 3 H, cyclopropyl), 1.29 (d, methyl, J = 5.6 Hz); uv λ_{max} (hexane) 230 nm (ϵ 10 800), 240 (6950), 260 (5820), 285 (1250), 292 (sh) (950), and 297 (290). **12:** ir (neat) 1390, 1365, 1230, 1100, 1092, 1020, 895 and 650 cm^{-1}; NMR (CCl_4) δ 7.4–6.6 (m, benzo) and 6.88 (d, $H_{3'}$, $J_{2'3'}$ = 5.5 Hz, 5 H together), 6.28 (d, $H_{2'}$, $J_{2'3'}$ = 5.5 Hz), 2.0–1.35 (m, 3 H, cyclopropyl), 1.27 (d, methyl, J = 5.6 Hz).

Anal. Calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.33; H, 7.77.

2,2-Dimethylspiro[cyclopropane-1,1′-indene] (15). Diazoindene,[14] obtained from 8.8 g (0.076 mol) of indene, was placed in an irradiation well fitted with a dry ice condenser, and 150 ml of isobutylene was condensed. The mixture was irradiated for 10 h through a Pyrex filter with a 450-W Hanovia Type L lamp while being cooled by a circulating methanol bath maintained at −5 to −15 °C. The isobutylene was then allowed to evaporate, and the reddish residue was distilled at 22 °C (0.07 mm) giving 2.0 g of distillate. GLC analysis on column B at 150 °C revealed that this contained **15** (82%), indene (5%), and an unidentified component (13%) with relative retention times (rrt) of 7:3:5, respectively. A 13% overall yield of **15** was achieved: ir (CCl_4) 3060, 2980, 2940, 2870, 1450, 1360, 1200, 1148, 1105, and 722 cm^{-1}; NMR (CCl_4) δ 7.45–7.0 (m, 4 H, benzo), 6.81 (d, $H_{3'}$, $J_{2'3'}$ = 5.6 Hz), 6.31 (d, $H_{2'}$, $J_{2'3'}$ = 5.6 Hz), AB quartet at 1.72 and 1.53 (cyclopropyl, J = 4.5 Hz), 1.42 (s, 6 H, methyl).

Anal. Calcd for $C_{13}H_{14}$: C, 91.76; H, 8.23. Found: C, 91.54; H, 8.18.

1-Alkyl- and 1-Allylindenes. General Procedure. Indene was added to a solution of sodium in liquid ammonia, followed by the dropwise addition of alkyl or allyl bromide. After workup, the reaction mixture was stirred for 30 min at −78 °C and quenched by the addition of 30 ml of pentane and 90 ml of saturated aqueous NH_4Cl. After evaporation of the ammonia, the pentane was removed by rotary evaporation, and the residue was distilled.

1-Isopropylindene (18a). The reaction of 58 g (0.50 mol) of indene, 8.1 g (0.35 g-atom) of sodium, and 73.5 g (0.60 mol) of isopropyl bromide in 500 ml of ammonia gave a yellow oil which was distilled [64 °C (0.9–1.2 mm)] to give 29.8 g (45%) of a 99:1 mixture of 1- and 3-isopropylindene. These isomers had GLC rrt values of 0.37 and 0.55, respectively, on column F at 120 °C. Isomer **18a** was purified on column C at 100 °C and displayed the following spectral data: ir (neat) 2880, 1460, 1390, 1370, and 775 cm^{-1}; NMR (CCl_4) δ 7.18 (m, 4 H, benzo), AB quartet at 6.72 and 6.32 (H_3 and H_2, J_{23} = 5.8 Hz, $J_{12} \approx J_{13} \approx$ 1.7 Hz), 3.28 (m, H_1), 2.18 (m, isopropyl methine), 1.00 (d, 3 H, methyl, J = 6.8 Hz), 0.58 (d, 3 H, methyl, J = 6.8 Hz).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.22; H, 9.19.

1-*n*-Propylindene (18b). The reaction of 20.8 g (0.18 mol) of indene, 2.4 g (0.11 g-atom) of sodium, and 26.4 g (0.21 mol) of *n*-propyl bromide in 150 ml of ammonia gave an oil which was distilled [45–46.5 °C (0.08 mm)] to afford 13.1 g (66%) of a 92:8 mixture of 1- and 3-*n*-propylindene which had GLC rrt values of 0.68 and 1.00, respectively, on column F at 120 °C. Isomer **18b** was purified on column B at 100 °C and displayed the following spectral data: ir (neat), 2930, 2860, 1370, 1355, 938, 880, 865, 770, 738, and 710 cm^{-1}; NMR (CCl_4) δ 7.17 (m, 4 H, benzo), AB quartet at 6.69 and 6.38 (H_3 and H_2, J_{23} = 5.8 Hz, $J_{12} \approx J_{23} \approx$ 1.8 Hz), 3.5–3.2 (m, H_1), 2.0–1.0 (m, 5 H, methylene), 0.89 (m, 3 H, methyl).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.18; H, 9.15.

1-Allylindene (17c). The reaction of 20.8 g (0.18 mol) of indene, 2.3 g (0.10 g-atom) of sodium, and 13.4 g (0.11 mol) of allyl bromide in 150 ml of ammonia gave, after distillation [45–55 °C (0.07 mm)], 1.27 g (82%) of a 91:9 mixture of 1- and 3-allylindene. These isomers had GLC rrt values of 0.68 and 1.29, respectively, on column F at 120 °C. Isomer **17c** was purified on column B at 100 °C and displayed the following spectral data: ir (neat), 3070, 1645, 1455, 998, 915, 775, 765, 745, 730, 715 cm^{-1}; NMR (CCl_4) δ 7.18 (m, 4 H, benzo), AB quartet at 6.71 and 6.37 (H_3 and H_2, J_{23} = 5.7 Hz, $J_{12} = J_{13}$ = 1.7 Hz), 6.2–5.4 (m, 1 H, allyl olefinic), 5.2–4.8 (m, 2 H, terminal-methylene), 3.38 (broadened t, $H_{1'}$, J = 7 Hz), 2.8–1.8 (m, methylene).

Anal. Calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.48; H, 7.74.

3-Alkyl- and 3-Allylindenes. Mixtures of 1- and 3-alkyl- or allylindenes could be converted essentially completely to the 3-alkyl or 3-allyl isomer by treatment with base. Typically, 2 g of the above mixture of 1- and 3-propylindene was added dropwise at room temperature to a solution of 0.2 g of KO-*t*-Bu in 25 ml of dimethyl sulfoxide (Me_2SO). After stirring for about 1 h, the reaction mixture was quenched by the sequential addition of 50 ml of saturated aqueous NH_4Cl, 40 ml of H_2O, and 50 ml of pentane. The organic layer was washed with water and dried ($MgSO_4$). The 3-propyl isomer (**17b**) was obtained in >99% purity and 56% yield upon removal of the solvent and distillation of the residue and was purified by GLC on column C at 100 °C. Compounds **17a** and **17c** were obtained in a similar fashion.

3-Isopropylindene (17a). Ir (neat) 2890, 1479, 1405, 1395, 1270, 1018, 970, 918, 780, 770, and 720 cm^{-1}; NMR (CCl_4) δ 7.22 (m, 4 H, benzo), 6.03 (broad s, H_2), 3.12 (broad s, 2 H, H_1), 2.85 (m, 1 H, isopropyl, J = 6.8 Hz), 1.23 (d, 6 H, methyl, J = 6.8 Hz).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.00; H, 9.20.

3-*n*-Propylindene (17b). Ir (neat) 2940, 2920, 1600, 1400, 1260, 1170, 1110, 960, and 768 cm^{-1}; NMR (CCl_4) δ 7.18 (m, 4 H, benzo), 6.02 (broadened s, H_3), 3.16 (apparent q, 2 H, H_1, $J_{12} = J_1$, propyl = 1.8 Hz), 2.45 (complex t, 2 H, allylic, $J \sim 7$ Hz), 1.58 (complex sextet, 2 H, $J \sim 7$ Hz), 0.97 (complex t, 3 H, $J \sim 7$ Hz).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.30; H, 9.10.

3-Allylindene (17c). Ir (neat) 3090, 2910, 1650, 1470, 1400, 995, 970, 915, 770, and 720 cm^{-1}; NMR (CCl_4) δ 7.18 (m, 4 H, benzo), 6.07 (broadened s, H_2), 6.3–5.6 (m, 1 H, olefinic), broadened d at 5.08 and 5.05 (2 H, terminal methylene), 3.15 (broad s, 4 H, H_1 and allylic).

Anal. Calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.44; H, 7.63.

1-Isopropylindan (16a) and 1-*n*-Propylindan (16b). The mixtures of 1- and 3-alkylindenes described above were dissolved in 50 ml of ethanol and hydrogenated at 37 psi over Pt (from Pt_2O) in a Parr apparatus. *n*-Propyl- and isopropylindene (2.4 and 2.0 g, respectively) gave quantitative yields of the corresponding indans. The latter could be purified on column B or C at 80 °C. **16a:** ir (neat) 1465, 1390, 1370, 755, and 740 cm^{-1}; NMR (CCl_4) δ 7.07 (broadened s, 4 H, benzo), 3.25–2.65 (m, 3 H, H_1 and H_3), 2.3–1.6 (m, 3 H, H_2 and isopropyl methine), 0.96 (d, 3 H, J = 6.7 Hz), 0.77 (d, 3 H, J = 6.7 Hz).

Anal. Calcd for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.71; H, 10.05.

16b: ir (neat), 1450 and 745 cm^{-1}; NMR (CCl_4) δ 7.07 (broadened s, 4 H, benzo), 3.3–2.7 (m, H_1), 2.78 (apparent t, 2 H, H_3, line separation ~7 Hz), 2.5–1.1 (m, 6 H, H_2 and isopropyl methylene), 0.95 (m, 3 H, methyl).

Anal. Calcd for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.76; H, 10.08.

Preparative Scale Reductive Cleavage of 11 and 12. A 63:37 mixture of *syn*- and *anti*-2-methylspiro[cyclopropane-1,1′-indene] (**11** and **12**) (25 g, 0.16 mol) was added to a solution of 11 g (0.64 g-atom) of lithium in liquid ammonia and stirred for 2 h. After quenching with 100 ml of saturated aqueous NH_4Cl, the ammonia was allowed to evaporate, and the yellow residue was taken up in pentane. The solvent was removed under vacuum, and the residue was flash distilled to afford 15.2 g (60%) of product. Products **16–18** were isolated by GLC on column B at 80 °C and (for **17c**) on column G at 95 °C. Relative yields are given in Table I. GLC rrt values on column F at 120 °C were: **16a,** 0.45; **16b,** 0.55; **16c,** 0.68; **17a,** 0.82; **17b,** 1.00. Isomers **11** and **12,** which were not present under these conditions, have a value of 1.4.

To test for the possible interconversion of **11** and **12,** a similar reaction mixture obtained after 5 min reaction time was injected on a 0.375 in. (o.d.) × 0.25 m du Pont Zorbax ODS liquid chromatography column (70 °C, 40% MeOH/H_2O, 2000 psi). Samples of recovered **11** and **12** both showed an unchanged isomeric purity (≥97%) after being subjected to the reductive cleavage conditions.

Analytical Scale Reductive Cleavages of 11 and 12. The product distributions described in Table I were obtained by running the reductive cleavage reaction on a small scale. Product distributions were obtained by GLC analysis on column D at 65–70 °C. Typically, 4 ml of anhydrous NH_3 was condensed into a test tube equipped with dry ice condenser and a side arm. Freshly cut, oxide-free lithium metal (8.4 mg, 1.2 mg-atoms) was dissolved, followed by 10 μl of **11, 12,** or a mixture of **11** and **12** (0.06 mmol) and 10 μl of undecane (internal standard). A mixture of 10 μl of a 63:37 sample of **11** and **12** in 0.25 ml of liquid ammonia was homogeneous at room temperature, and the relative intensities of the doublets at δ 5.98 and 6.28 remained unchanged on cooling the sample to −36 °C. The reaction mixture was stirred for 1 h and then quenched by the addition of three drops of saturated aqueous NH_4Cl. After the ammonia had evaporated, the residue was taken up in 100 μl of pentane and analyzed by GLC. Peak areas were determined by electronic integration. Identical procedures were employed for sodium reductions.

Reaction of *syn*- and *anti*-2-Methylspiro[cyclopropane-1,1′-indene] (11 and 12) with Alkali Metal Amides. (1) Lithium Amide. To a solution of 4.2 mg (0.60 mg-atom) of fresh lithium metal in 2 ml of refluxing ammonia in the side-arm tube described above was added a few crystals of ferric chloride. The solution was allowed to stir until the deep blue color of the dissolved metal had completely faded. A 63:37 mixture of **11** and **12** (5 μl, 0.03 mmol) and 5 μl of undecane (internal standard) was injected, and, after stirring for 1 h, the mixture was quenched by the addition of five drops of saturated aqueous NH_4Cl. The ammonia was allowed to evaporate, and the organic residue was taken up in 100 μl of pentane and analyzed by GLC on column D at 65–70 °C. Recovery of starting material was ca. 92%, and no reduced or ring-opened products were detected.

(2) Sodium Amide. $NaNH_2$ [45 mg (1.2 mg-atoms)] was dissolved in 10 ml of refluxing ammonia in the side arm tube described above. A 63:37 mixture of **11** and **12** (10 μl, 0.06 mmol) and 10 μl of undecane were injected. The reaction mixture was stirred for 1 h before being quenched and analyzed as above. The product mixture (94% material balance) consisted of ~85% unchanged **11** and **12,** ~14% **17c** (by retention time), and two minor unidentified products (~2% and <1%).

Spiro[cyclopropane-1,1′-indan] (19). Spiro[cyclopropane-1,1′-indene] (**14**)[13] (1 g, 7.0 mmol) was dissolved in 25 ml of absolute ethanol and stirred over Pt (from 90 mg of PtO_2) under a positive pressure of hydrogen. After 5 h, ~120 ml (5.3 mmol) of hydrogen had been taken up. The reaction mixture was diluted with 100 ml of distilled H_2O, and the resulting solution was extracted three times with 100 ml of pentane. The combined extracts were stripped of solvent by rotary evaporation. Analysis and purification of the products (obtained in nearly quantitative yield) on column E at 90 °C showed 1-ethylindan (10%), **19** (24%), 1-ethylindene (5%), and **14** (60%) with rrt values of 1.0:1.8:2.2:3.8, respectively. Spiro[cyclopropane-1,1′-indene] (**14**): ir (neat) 3075, 3055, 3010, 1455, 1430, 1290, 1083, 1050, and 870 cm^{-1}; NMR (CCl_4) δ 7.4–6.7 (m, 5 H, benzo), AB quartet at 6.78 and 6.03 ($H_{3'}$ and $H_{2'}$, $J_{2'3'}$ = 5.6 Hz), 1.48 (broadened s, 4 H, cyclopropyl).

Anal. Calcd for $C_{11}H_{10}$: C, 92.96; H, 7.04. Found: C, 92.82; H, 7.11.

Spiro[cyclopropane-1,1′-indan] (**19**): The NMR and ir spectra were identical with those reported in the literature.[23]

Anal. Calcd for $C_{11}H_{12}$: C, 91.66; H, 8.34. Found: C, 91.72; H, 8.54.

1-Ethylindan: NMR (CCl_4) δ 7.13 (broad s, 4 H, benzo), 3.2–2.7 (m of 4 major lines, 3 H, H_1 and H_3), 2.6–1.2 (m, 4 H, H_2 and methylene), 0.98 (t, 3 H, methyl, J = 7 Hz). 1-Ethylindene was identified on the basis of an AB quartet at δ 6.25 and 6.78 (H_2 and H_3, $J_{23} \approx 6$ Hz) and a 7 Hz triplet at 1.22 (methyl) in the NMR spectrum of partially purified material.

Kinetic Studies of Reductive Cleavages. Reductive cleavages of **19** and of a 63:37 mixture of **11** and **12** by a tenfold molar excess of alkali metal in refluxing liquid ammonia were conducted by the method described above for the analytical cleavages of **11** and **12** except that the reaction times were varied (Table II). The product distributions obtained were identical with those in Table I.

Relative Rates of Cleavage of *syn*- and *anti*-2-Methylspiro[cyclopropane-1,1′-indene] (11 and 12) by Lithium or Sodium in Ammonia. A 63:37 mixture of **11** and **12** (250 μl) was treated for 45 min with a tenfold molar excess of lithium under the conditions described above for the analytical cleavages of **11** and **12.** GLC analysis after quenching and work-up of the reaction mixture showed about 90%

Table II. Kinetic Data for Reductive Cleavages of **11, 12,** and **19**

Starting material	Alkali metal	Reaction s time,	Fraction of starting material recovered
11 and **12** (63:37)	Na	15	0.88
		30	0.79
		180	0.26
		240	0.17
		360	0.077
19	Na	60	0.95
		900	0.68
		1500	0.46
		3600	0.21
11 and **12** (63:37)	Li	600	0.53
		1800	0.15
		3600	0.03

destruction of the starting material. Unchanged **11** and **12** were isolated by GLC on column B at 65 °C. NMR analysis showed a 65:35 ratio of **11** and **12.** Similarly, recovery of **11** and **12** from a reaction with sodium in ammonia (85% destruction of starting material) afforded a 65:35 mixture of these isomers.

Product Stability under Reductive Cleavage Conditions. To a solution of 0.17 g (7.4 g-atom) of sodium in 10 ml of ammonia was injected 50 μl (~0.3 mmol) of alkyl- or allylindene. After stirring for 1 h, the reaction was quenched and worked up as described above for the synthesis of alkylindenes. The products were analyzed on GLC column D at 65 °C. The product mixture from the treatment of **17a** consisted of 74% 1-isopropylindan (**16a**) and 26% **17a,** whereas the product mixture from the cleavage of **17c** consisted of 20% 1-*n*-propylindan (**16b**), 76% 1-allylindan (**16c**), 2% 3-allylindene (**17c**), and two unidentified products each formed in <2% yield. When lithium was substituted for sodium, **17a** produced 87% **16a** and 11% **17a,** whereas **17c** produced 21% **16b,** 72% **16c,** 5% **17c,** and 2% of an unidentified product.

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Synthesis of Electrically Conductive Organic Solids

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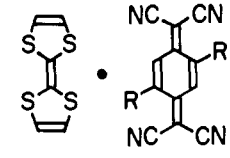
Abstract: Over 80 electrically conductive charge-transfer complexes are reported. Donor structures include tetrathioethylenes, dithiodiaminoethylenes, dithiodiselenoethylenes, tetraaminoethylenes, azines, aromatic hydrocarbons, and aromatic heterocycles. Acceptor structures include substituted tetracyanoquinodimethanes, metal dithiolates, cyanocarbons, and nitro compounds. A novel dithiodiselenoethylene synthesis is reported. A rather general electrochemical technique for growing high-quality single crystals is discussed, and compaction resistivities are compared with corresponding single crystal values. Redox potentials are reported for a number of donors and acceptors.

Introduction

The room-temperature electrical conductivity of the tetrathiofulvalene–tetracyanoquinodimethan (TTF·TCNQ) charge-transfer complex **1** is comparable with that of graphite.[1,2] Lowering the temperature to roughly 60 K increases conductivity ten- to 500-fold,[1,2] the magnitude of this enhancement being a point of scientific controversy.[3-8]

In the context of materials analogous to TTF·TCNQ, the need for planar molecules capable of close, highly ordered packing and of stable radical ion configurations seems clear. But otherwise the detailed molecular requirements for high conductivity are poorly established and have been the subject of speculation in the literature. High symmetry,[1] high polarizability,[1,2,9,10] small molecular size,[10] high acceptor electron affinity,[10] low donor ionization potential,[10] partial electron transfer,[10,11-14] and small separation between first and second redox potentials[10] are among the factors felt to favor high conductivity. The roughly 80 conductive organics reported in



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