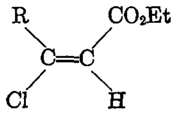
minimum. We feel that the method gives a more accurate picture of the isomer ratio of the products of the reaction than previous procedures. We obtained similar results to those of Jones[2] when the products of the reaction were isolated by distillation and the ratio was determined from the amounts of isolated *cis* and *trans* isomers.

It would therefore appear that the partial inversion of configuration observed by Jones[2] in the reaction of sodium benzenethiolate with the ethyl β-chlorocrotonates was due to thermal isomerization during the isolation of the product and is not inherent in the reaction. Our results show that there is no inversion of configuration of reactants during the reaction and also that the products are obtained with essentially retained configuration (>95%). It would thus seem that the mechanism advanced by Jones, *et al.*,[2] requires some modification. They suggest that inversion should take place when the grouping R is bulky. We synthesized the chloroalkenoate having



R = isopropyl, ethyl 3-chloro-4-methyl-2-pentenoate, and did not observe any inversion of configuration in the substitution reaction with sodium benzenethiolate. Thus, the reaction does not obey the simple steric hindrance factors they postulate. The mechanism advanced by Miller and Yonan,[4] in which they postulate inversion at a carbon atom adjacent to the reaction site to be faster than internal rotation, would agree with our facts. We assume the incoming nucleophile and the electron pair enter *trans* in the plane of the original π-orbital and the halide departs only when it is *trans* to the electron pair. It will thus be seen that, for retention to occur, the halide ion needs only to rotate through 30° and the steric hindrance factors advanced by Jones, *et al.*,[2] are relatively unimportant. This would agree with the observed retention figures given in Table I and also the retention of configuration in the reaction of sodium benzenethiolate with ethyl 3-chloro-4-methyl-2-pentenoate.

It must, however, be stated that the experimental evidence for the two assumptions given above is inadequate, and thus further work is necessary before any final conclusion may be made about the mechanism of the reaction.

Experimental Section

The configuration of the products was determined using infrared spectra[2] in the region of 800–1000 cm.$^{-1}$ and by determination of the vinylic proton and vinylic methyl chemical shifts with a Varian A-60 n.m.r. spectrometer[3] operating at a frequency of 60 Mc.p.s. Samples were run in carbon tetrachloride at approximately 10% concentration using tetramethylsilane as an internal standard.

The products were obtained by the reaction of the appropriate ethyl chloroalkenoate (*ca.* 10% excess) in alcohol with the sodium salt of the thiol in alcohol. The solutions were mixed at 3° and left to stand at 3° for 4 hr. The mixture was then poured into water and the product was either filtered off or extracted with peroxide-free ether.

The preparation and physical data of the compounds discussed in this paper have been described elsewhere.[8]

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Magnetic Nonequivalence of Methylene Group Protons in 1,2-Disubstituted Ferrocenes

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Diastereomeric[2] methylene protons adjacent to an element of dissymmetry such as an asymmetric atom[3,4] or a twisted biphenyl[2,5] have been reported to show magnetic nonequivalence in a variety of solvents and over a range of temperatures. Uncertainty has existed, however, as to the relative importance of conformational effects *vs.* the "intrinsic asymmetry" of the molecule. Somewhat opposing views have been presented recently by Roberts,[4] *et al.*, and Gutowsky, *et al.*[6]

A recent n.m.r. investigation[7] of a series of *ortho*- and *meta*-substituted N,N-dimethylbenzylamines has demonstrated that an asymmetric group in the *ortho* or *meta* side chain in every case was accompanied by magnetic nonequivalence of the methylene group protons in the amine side chain. Those benzylamines which did not bear an asymmetric group exhibited an apparent methylene singlet. These results are supported by n.m.r. spectra of two phthalans[8] related to the compounds previously studied. The present report concerns the n.m.r. spectra of the 1,2-disubstituted ferrocene analogs of five of the previously studied symmetrical *ortho*-substituted benzene derivatives, their formulas being I–V. As expected,[7,8] all five ferrocenes displayed magnetically nonequivalent methylene-group protons, providing a novel demonstration of the asymmetry of these ferrocenes.[9] The results reveal a difference in chemical shift for the expected[7,8] nonequivalent methylene-group protons as large as 1 order of magnitude greater than in the corresponding *ortho*-substituted benzene compounds. Conformational effects which are peculiar to ferrocenes[10] do not allow an unambiguous assignment of the origin of the observed nonequivalence.

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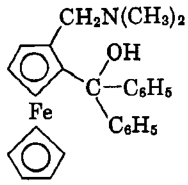

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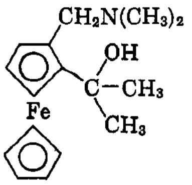

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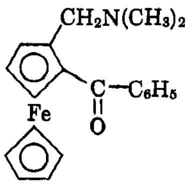

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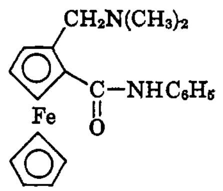

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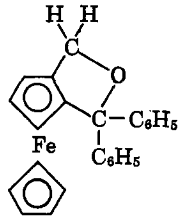

V

Results and Discussion

The n.m.r. results are summarized in Table I, chemical shifts being reported in cycles per second downfield from the internal TMS standard. In Table I protons 1 and 2 refer to the methylene group protons and ν_1 and ν_2, respectively, are their calculated[11] chemical shifts. The quantity $J_{1,2}$ is the measured coupling constant; $\delta_{1,2}$ is the difference in the 1,2-proton chemical shifts. For each compound and in every solvent protons 1 and 2 were magnetically nonequivalent, while the N-methyl protons appeared equivalent. In addition, for compound II the C-methyl protons were nonequivalent.

Table I[a]

N.m.r. Data for 36° and 60 Mc.

Compd.	Solvent	ν_1	ν_2	$\delta_{1,2}$	$J_{1,2}$
I	$CDCl_3$	159.2	218.0	58.8	13.4
	CCl_4	156.0	224.5	68.5	13.2
	CH_3CN	158.0	222.1	64.1	13.5
	CH_3COCH_3	161.9	228.5	66.6	13.5
	C_6H_6	147.6	222.6	75.0	13.2
	$(CH_3)_2CHCOOCH_3$	160.1	228.0	67.9	13.1
	C_6H_5CN	158.0	224.3	66.3	13.5
	RNH_2[b]	158.4	222.0	63.6	13.5
II[c]	$CDCl_3$	156.8	242.3	85.5	12.6
	CCl_4	151.3	241.0	89.7	12.3
	C_6H_6	145.9	244.2	98.3	12.7
III	$CDCl_3$	207.0	258.4	51.4	13.4
	CCl_4	203.2	262.3	59.1	13.1
	C_6H_6	214.4	284.6	57.2	13.4
IV	$CDCl_3$	177.1	247.9	70.8	12.8
	CH_3COCH_3	171.1	260.0	88.9	12.6
	CH_3CN	181.6	253.1	71.5	12.5
	C_6H_6	150.5	231.9	81.4	12.9
	C_6H_5CN	161.5	245.9	74.4	12.5
	$C_6H_5CH_3$	152.9	233.7	80.8	12.8
V	$CDCl_3$	265.8	286.0	20.2	11.0
	CH_3COCH_3	261.0	287.8	26.8	10.9
	C_6H_6	262.8	277.9	15.1	10.3

[a] See the text for the meaning of the symbols. The data are all in cycles per second, TMS being used as an internal reference. Coupling constants and chemical shifts are expressed to the nearest 0.1 c.p.s. Each coupling constant value is the arithmetical mean of all data taken. Single measurements for each constant varied from the reported value by as much as a few tenths of a cycle per second. [b] $(CH_3)_2CHCH_2C(CH_3)_2NH_2$. [c] Relative chemical shifts for the nonequivalent C-methyl group protons are 21.0, 17.5, and 16.0 ± 0.5 c.p.s. in $CDCl_3$, CCl_4, and C_6H_6, respectively.

The chemical shift differences observed for the methylene group protons are large and constitute a relatively novel instance of magnetic nonequivalence in a system of low symmetry. From previous results[7,8] on benzene analogs of I–V, magnetic nonequivalence of the methylene group protons was expected. Nevertheless, the compounds reported are a significant addition to the number of 1,2-disubstituted ferrocenes previously reported[12,13] which are capable of exhibiting nonequivalent methylene- or *gem*-dimethyl-group protons. Since not all reported asymmetric 1,2-disubstituted ferrocenes show magnetically nonequivalent protons, the present results could be important in establishing the origin of this type of nonequivalence. A firm basis for assigning the conformational preferences of compounds I–V is not yet available. Consequently, a reliable decision as to the probable cause of the observed nonequivalence cannot be made.

Experimental Section

The compounds were prepared and characterized as part of another investigation.[14] Compounds I–IV are 2 derivatives of N,N-dimethylaminomethylferrocene. Compound V is the ferrocene analog of 1,1-diphenylphthalan. Spectra were obtained on a Varian A-60 n.m.r. spectrometer equipped with a Varian V-6057 variable temperature accessory, TMS being used as an internal standard. Solvents were reagent grade or better. Concentrations were 0.2 *M* and the probe temperature was 36 ± 1°. A minimum of two spectra were run for each solution.

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Small Charged Rings. VIII. Isolation and Stereochemistry of Acyl Aziridinium Salt Intermediates[1,2]

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Urbana, Illinois

Received July 7, 1965

The early postulate of aziridinium salt intermediates to explain certain rearrangements and conversions of

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[1] For preceding article in this series, see N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **30**, 821 (1965).

[2] This investigation was supported by a research grant (USPHS-RG5829, afterward designated GM-05829) from the National Institutes of Health, U. S. Public Health Service, to whom we are pleased to acknowledge our thanks.

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