[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Aromatic Silicon Systems. II. The Silacyclopentadienide Anion

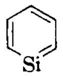
BY ROBERT A. BENKESER, RICHARD F. GROSSMAN AND GARTH M. STANTON

RECEIVED JULY 20, 1962

Silacyclopentadiene has been found to react directly with potassium forming hydrogen and potassium silacyclopentadienide. Comparison of the nuclear magnetic resonance spectra of silacyclopentadiene and potassium silacyclopentadienide provides graphic evidence that it is the silanic hydrogens which are replaced by the metal in this reaction. Significantly, divinylsilane (the open chain analog of silacyclopentadiene) does not react with potassium at any appreciable rate under comparable conditions. This suggests that resonance stabilization of the silacyclopentadienide anion is providing a driving force for this reaction. Potassium silacyclopentadienide reacts with bromobenzene forming a mixture of 1-phenylsilacyclopentadiene and 1,1-diphenylsilacyclopentadiene. The structure of the latter two compounds was established by reducing them catalytically to phenylated silacyclopentanes which, in turn, could be prepared by unequivocal routes. Potassium silacyclopentadienide is colored in tetrahydrofuran solutions and possesses a spectrum which is quite similar to potassium cyclopentadienide in the visible region. All of the foregoing observations point to some measure of resonance stabilization in the silacyclopentadienide ring system, suggesting that the "Hückel rule" will enjoy some success in predicting aromatic character for certain silicon ring systems.

The feasibility of incorporating the silicon atom into an aromatic system has intrigued both the theoretical and synthetic chemist for many years. Several unsuccessful attempts to prepare aromatic silicon systems have been reported.[1]

With the heralded success of the Hückel[2] rule in predicting aromaticity in carbon compounds, it seemed desirable to test the applicability of this concept in the silicon series. Silicon compounds, which, according to the Hückel rule, might be expected to possess aromatic character include the traditionally elusive silabenzene (I), the silacyclopentadienide anion (II) and the silatropylium cation (III). Accordingly, a research program was inaugurated in our laboratory designed to explore the possibility of synthesizing aromatic silicon compounds of types I, II and III. In this paper we are reporting the successful synthesis and characterization of the silacyclopentadienide[3] anion (II). We believe this represents the first example of an aromatic silicon system.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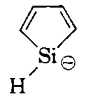
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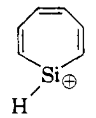
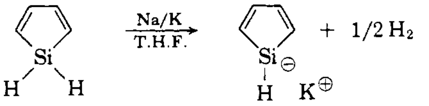

III

Results

It is well known that cyclopentadiene can be made to react directly with alkali metals to form the cyclopentadienide anion.[4] Hydrogen is the other product of this reaction. With silacyclopentadiene now readily accessible,[5] it was of extreme interest to compare the reaction of this compound with alkali metal.

When silacyclopentadiene was treated with potassium in either anhydrous ether or tetrahydrofuran, a colored solution was formed and a gas was evolved. A mass spectrographic analysis of this gas indicated that it was hydrogen. The volume of hydrogen, as measured in a modified "Grignard machine," was 91% of the theoretical in accord with the equation



Both the cyclopentadienide anion and its silicon analog have a greenish color in dilute solutions of tetrahydrofuran and orange in concentrated solutions. This is not surprising since both species have a markedly similar absorption spectrum in the visible region (see Table I). Since both absorb at each end of the visible spectrum, it might be expected that solvent effects could give rise to a variety of colors.

TABLE I

ULTRAVIOLET SPECTRA OF CONJUGATED UNSATURATED SILACYCLIC COMPOUNDS[a]

	$\lambda_{\max}^{\text{ether}}$, mμ	log $\epsilon_{\max}$
Silacyclopentadiene	232	3.8
1,1-Dichlorosilacyclopentadiene	228	4.2
1,1-Diphenylsilacyclopentadiene	230	4.0
	248	3.7
Potassium silacyclopentadienide[b]	415	1.0
	750	1.5
Potassium cyclopentadienide[b]	410	1.0
	780	1.5

[a] These data were obtained on a Bausch and Lomb Spectronic 505. Concentrations were of the order of 10^{-4} molar. [b] The absorptions given are for the visible region only. Typical diene absorption also is observed at lower wave lengths.

Nuclear magnetic resonance proved to be a powerful tool in establishing the structure of potassium silacyclopentadienide. The n.m.r. spectrum of silacyclopentadiene itself showed doublet C–H peaks at 2.96 τ and an Si–H peak at 4.12 τ with relative areas of 1:1:1 (see Table II). This is quite in keeping with the expectation of two similar hydrogen atoms at both the α- and β-positions as well as two more attached to the silicon atom. On the other hand, the n.m.r. spectrum of the potassium salt showed C–H peaks at 2.70 and 2.90 τ, respectively, as well as an Si–H peak at 3.95 τ (relative areas of 1:1:0.5). Clearly the hydrogen

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[1] For example see: R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954); A. F. Plate and N. A. Belikova, *J. Gen. Chem. U.S.S.R.*, **27**, 2529 (1957) (Eng. trans.).

[2] E. Hückel, *Z. Physik*, **70**, 204 (1931).

[3] For a preliminary report of this material see R. A. Benkeser, R. F. Grossman and G. M. Stanton, *J. Am. Chem. Soc.*, **83**, 5029 (1961).

[4] J. Thiele, *Ber.*, **34**, 68 (1901); see also E. O. Fischer, *et al.*, *Z. Naturforsch.*, **8b**, 217, 444 (1953).

[5] See Paper I in this series: R. A. Benkeser, R. F. Grossman and G. M. Stanton, *J. Am. Chem. Soc.*, **84**, 4723 (1962).

Table II

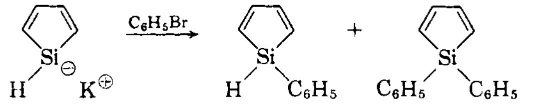
Nuclear Magnetic Resonance Spectral Data[a]

Compound	Vinyl CH	Si–H
1,1-Dichlorosilacyclopentadiene	2.48	
Silacyclopentadiene	2.96	4.12
Potassium silacyclopentadienide[b]	2.70 2.90	3.95
Trichlorovinylsilane[c]	3.75	
Dichlorodivinylsilane	3.5	
Divinylsilane	3.8	3.95

[a] The values given are "tau" values based upon tetramethylsilane as an internal standard. [b] This spectrum was taken in THF solution. [c] This value is taken from Varian Associates Spectra Catalog, 1962. Clearly the vinyl H's are not resolved in the three vinylsilanes listed.

which was replaced by the metal was attached originally to the silicon atom.

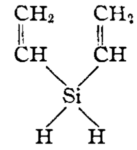
Chemical evidence for the presence of the silacyclopentadienide anion was obtained by treating it with bromobenzene in tetrahydrofuran. A mixture of 1-phenylsilacyclopentadiene and 1,1-diphenylsilacyclopentadiene was formed in about 60% yield. The latter compound could be isolated from the mixture at low temperatures and melted at 55–56° (mixed m.p. 55–56°). Identification of these two products was readily achieved by hydrogenating them catalytically to 1-phenylcyclopentane and 1,1-diphenylcyclopentane, respectively. Authentic samples of the latter two materials had identical infrared spectra and retention times (vapor phase chromatography) as the products obtained from the anion reaction with bromobenzene.



Coupling of the anion with bromobenzene very likely occurred *via* a benzyne intermediate, although no attempt was made to determine the mechanism of this reaction. It should be noted that there is precedent for such a reaction in organosilicon chemistry. Triphenylsilylpotassium couples readily with bromobenzene forming tetraphenylsilane in good yield.[6]

The 1,1-diphenylsilacyclopentadiene undoubtedly arises from a metalation of 1-phenylsilacyclopentadiene. The hydrogen attached to the silicon atom in the latter compound should be more acidic (due to the −I effect of the phenyl group) than the corresponding ones in silacyclopentadiene. Hence, it should react quite rapidly with both alkali metal and the anion derived from silacyclopentadiene itself.

Of extreme significance was the observation that divinylsilane IV, the open-chain analog of silacyclopentadiene, did not react with potassium in tetrahydrofuran at any appreciable rate. Several parallel experiments were carried out in which the divinylsilane and silacyclopentadiene were treated with the metal in tetrahydrofuran under exactly comparable experimental conditions. Hydrogen evolution was very noticeable in the case of silacyclopentadiene while its open chain analog (divinylsilane) seemed not to react at all. When bromobenzene was added to each of these reaction mixtures, a noticeable change occurred in the case of the cyclic anion, which resulted in the ultimate isolation of the mono- and diphenylated products. Only unchanged bromobenzene could be recovered from the divinylsilane mixture. One can only conclude that the driving force, which permits the facile conversion of silacyclopentadiene to its anion, is not provided, at least to the same extent in the case of divinylsilane.



IV

Since divinylsilane had not been reported previously to our knowledge, we felt compelled to prove the structure of this compound since its subsequent treatment with alkali metal was a pivotal experiment. The structure proof was readily achieved by hydrogenating the compound catalytically to the known diethylsilane.[7] The material prepared in this fashion proved identical in every respect with an authentic sample prepared by reducing diethyldichlorosilane with lithium aluminum hydride. There can be no doubt, therefore, that it was divinylsilane which failed to react at an appreciable rate with potassium.

Discussion

The "aromaticity" of the 6π-electron system of the cyclopentadienide anion is usually conceded.[8] The question now arises as to whether the properties of the silacyclopentadienide are such as to merit for it the classification of "aromatic."

It is generally agreed that a closed conjugated π-system, which possesses unusual stability or properties that cannot be described adequately by a single formula, possesses aromaticity. Thus aromaticity is inescapably bound to resonance, or the extent to which a molecule possesses delocalization energy. The vital question, then, is: to what extent or degree does the silacyclopentadienide anion possess electron delocalization or resonance energy?

At present we feel there are three experimental observations which point to *some* resonance stabilization in the silacyclopentadienide system. (1) The similarity of the ultraviolet spectra of the silacyclopentadienide and cyclopentadienide anion systems; this is usually taken as an indication of similar orbital energies.[8a] (2) The color which the silacyclopentadienide possesses in both ether and tetrahydrofuran. It has been recognized for a long

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(6) R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951); H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951).

(7) J. S. Peake, W. H. Nebergall and Y. T. Chen, *ibid.*, **74**, 1526 (1952).

(8) See Chapter III by P. L. Pauson in "Non Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

(8a) *Added in Proof.*—In a private communication, Dr. Stewart McLean (Univ. of Toronto) has informed us that he is currently investigating the hypothesis that the color traditionally credited to the cyclopentadienide anion is, in reality, caused by oxidation products. If this interesting idea proves correct, obviously our ultraviolet comparisons and the arguments for aromaticity of the silacyclopentadienide anion derived from them, would not be valid.

time that organometallics containing a carbon-metal σ-bond are highly colored only when the negative charge of the anion can be resonance-stabilized. Classic examples of this color phenomenon are phenylisopropylpotassium (red), triphenylmethylsodium (red) and benzyllithium (red-brown). (3) The observation that there is an enormous difference in the rate of reaction of silacyclopentadiene and its open-chain analog, divinylsilane, with alkali metal. Clearly the hydrogen atom joined to the silicon in the cyclic system is more readily displaced. While greater steric effects in the divinylsilane system cannot be ruled out at the moment as an explanation for this rate difference, we are inclined to attribute it rather to the driving force provided by resonance delocalization in the cyclic anion.

Thiophene is one of the very few cyclic systems containing a "second-row" element which is unequivocally recognized to have considerable resonance energy (29–32 kcal./mole). Longuet-Higgins[9] has argued that the greater resonance energy of thiophene compared to furan (15 kcal./mole) indicates participation by sulfur d-orbitals. In a molecular orbital description of thiophene, it was proposed that the sulfur $3p_z$, $3d_{xz}$ and $3d_{yz}$ orbitals are hybridized to three directed orbitals, two of which are capable of strong π-overlap with adjacent carbon $2p_z$-orbitals. It seemed reasonable to apply these same considerations to silicon, since silicon d-orbital participation has been proposed in a number of different connections.[10] An LCAO-MO calculation based upon silicon d-orbital participation indicates a resonance energy of approximately 36 kcal./mole.[11] Thus, while the final answer to the question of resonance stabilization in the silacyclopentadienide anion must await some precise physical measurements (*e.g.*, X-ray analysis), qualitative evidence at the moment points to a substantial delocalization of charge in the cyclic system. Hence, it appears that the Hückel rule can be used with at least some measure of success in predicting aromaticity in the silicon series.

The n.m.r. spectra of silacyclopentadiene and its anion (see Table II) are worthy of some comment. It will be noted that both the α- and β-proton resonance of silacyclopentadiene have merged and appear at quite low field, 2.96 τ. Conversion to the anion causes only a slight shift to lower field for both the ring and silane hydrogens. A larger shift than the one actually observed might have been predicted. A possible explanation for the relatively small shift might be that a π-electron ring current is operative even in the parent silacyclopentadiene. It would seem possible for the π-electrons of the conjugated double bond system to overlap the vacant 3-d-orbitals of the silicon and thus make for a closed π-system. It will be recalled that such a picture has been suggested for the thiophene ring. Interestingly, the n.m.r. spectrum of thiophene appears rather similar in shape to that of silacyclopentadiene with proton resonance again occurring at quite low field (2.81 and 2.96 τ).[12] Such a ring current would be, of course, impossible in cyclopentadiene itself Proton resonance occurs farther up field in this molecule—3.75 and 7.35 τ.[13] It is possible that only a modest increase in ring current occurs when the silacyclopentadiene is converted to its anion, and hence the small n.m.r. shift.

It should be noted that a similar phenomenon was noted when cycloöctatetraene was converted to its dianion with alkali metals.[14] The n.m.r. spectrum of both the dipotassium and dilithium cycloöctatetraenide were insignificantly displaced from the resonance of cycloöctatetraene itself. In this case it was suggested that an increase in proton shielding caused by the addition of electrons compensated for the displacement to low fields which might be expected because of an increase in ring current. A similar explanation might be valid for the case of silacyclopentadiene and its anion.

It must be emphasized that the preceding interpretative comments about the n.m.r. spectra of the silicon compounds are to be regarded as purely speculative at this time. The spectra of many more model compounds are needed for study before any truly valid conclusions can be drawn.

Experimental

Divinylsilane.—A sample of 15.5 g. (0.1 mole) of divinyldichlorosilane[15] (b.p. 119–120°) was added slowly to a stirred dispersion of 5 g. (0.13 mole) of lithium aluminum hydride in 100 ml. of dry diethyl ether. After stirring for 1 hour, water was added dropwise under nitrogen. After the ether layer was dried, the solvent was removed and the residue was fractionated on a Todd column. There was obtained 6.2 g. (65%) of divinylsilane boiling at 55° ($n^{25}\text{D}$ 1.4030).

Anal. Calcd. for C_4H_8Si: C, 57.06; H, 9.57. Found: C, 57.02; H, 9.75.

A sample of this product was hydrogenated catalytically over platinum. It adsorbed the theoretical amount of hydrogen and yielded diethylsilane (b.p. 56°, $n^{25}\text{D}$ 1.3904). The latter was identical in all respects (retention time, refractive index and infrared spectrum) with an authentic sample prepared by treating diethyldichlorosilane with lithium aluminum hydride.

Metalation of Silacyclopentadiene.—Potassium sand was prepared in benzene. The benzene was removed and purified tetrahydrofuran was added along with 0.5 g. (0.006 mole) of silacyclopentadiene. Excess alkali metal was removed at this point by amalgamation.[16] Excess bromobenzene was now added and the mixture was allowed to stand overnight. Upon hydrolysis and work-up, both 1-phenylsilacyclopentadiene and 1,1-diphenylsilacyclopentadiene could be isolated as a fluorescent oil in a combined yield of about 60%. The 1,1-diphenylsilacyclopentadiene could be isolated from this mixture at low temperatures as crystals melting at 55–56°. A mixed melting point with an authentic sample of this compound was undepressed.

When the fluorescent oil was dissolved in absolute ethanol and hydrogenated over platinum at room temperature and atmospheric pressure, a mixture of 1-phenylsilacyclopentane (see below) and 1,1-diphenylsilacyclopentane was obtained as shown by a comparison of their V.P.C. retention times with those of authentic samples.

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[9] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

[10] See, for example, "Organosilicon Compounds," by C. Eaborn, Butterworths Scientific Publications, London, Eng., 1960, p. 91.

[11] The method and calculations leading to this result will be published later.

[12] See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 64.

[13] G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[14] T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

[15] D. T. Hurd, *ibid.*, **67**, 1813 (1945).

[16] H. Gilman and co-workers, *ibid.*, **74**, 561 (1952).

The above experiment was repeated using divinylsilane instead of the silacyclopentadiene. All other variables were held constant, *e.g.*, concentrations, reaction time etc. It became immediately apparent that the rate of reaction of divinylsilane relative to silacyclopentadiene was exceedingly slow. Removal of the solvent (and divinylsilane) left behind a relatively pure sample of bromobenzene as shown by infrared and vapor phase chromatography. There was no trace of phenylated products as was the case with silacyclopentadiene.

1-Phenylsilacyclopentane.—One-half mole of phenylmagnesium bromide (from bromobenzene and magnesium) was added slowly to 77.5 g. (0.5 mole) of 1,1-dichlorosilacyclopentane in ether. After the addition, the mixture was stirred overnight; the precipitated salts were filtered off and the ether removed. The residue was distilled on a Todd column; 25 g. was obtained boiling at 89–90° (2.5 mm.). An additional 8.5 g. was collected at 91–92° (2.5 mm.). The total yield of 1-chloro-1-phenylsilacyclopentane was 33.5 g. (50%). Thirty grams (0.15 mole) of this material was immediately added dropwise to excess lithium aluminum hydride in ether and allowed to stir overnight. Then dilute hydrochloric acid was added until the salts coagulated. After these salts were filtered, they were washed with ether, and the ether removed. The residue was distilled and 11 g. of 1-phenylsilacyclopentane was obtained boiling at 95° (10 mm.), n^{25}_{D} 1.5358. An infrared spectrum of this material showed Si–H and Si-phenyl absorption. An additional 7.5 g. of product was obtained from this reaction boiling at 96–98° (10 mm.); total yield 18.5 g. (80%).

Anal. Calcd. for $C_{10}H_{14}Si$: C, 74.07; H, 8.64; Si, 17.07. Found: C, 74.07; H, 8.74; Si, 17.00.

Hydrogen Determination.—An apparatus was set up to measure hydrogen evolution quantitatively.[17]

Freshly prepared silacyclopentadiene (0.3 g., 0.0036 mole) was weighed out and injected by means of a syringe into a sodium–potassium alloy (0.1 g. of sodium, 0.6 g. of potassium) contained in a small amount of dimethyl ether or diethylene glycol or tetrahydrofuran. Gas evolution was immediate and vigorous. When reaction had ceased, the solution was heated briefly and allowed to cool. The arms of the manometer were then allowed to come to equilibrium. A total of 41.50 ml. of hydrogen[18] at 25° and 748 mm. was collected. This corresponds to a 91% yield of gas.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

[17] The apparatus used was essentially a modified "Grignard machine." See "Advanced Organic Chemistry" by L. F. Fieser and M. Fieser, Reinhold Publishing Corp., New York, N. Y., 1961, p. 422.

[18] Analysis of this gas was made in a Bendix Time-of-Flight Mass Spectrometer.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

Redistribution and Reduction Reactions of Alkoxysilanes

BY JOHN W. RYAN

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Strong bases have been found to catalyze the redistribution of alkyl, aryl, silyl and alkoxy groups attached to silicon. Alkali metals cause reduction of methoxy or phenoxy silicon compounds to form methyl or phenyl silicon compounds. This reduction reaction is a new method of forming carbon–silicon bonds.

The ability of tetra-substituted silanes to undergo disproportionation has long been recognized. Acidic catalysts such as aluminum chloride have been investigated. Russell[1] studied such systems and summarized the results of other investigators. Alkaline catalysts are also known to promote such reactions. Friedel and Ladenburg[2] showed that sodium or very likely the ethoxide ion promoted the disproportionation of triethoxysilane.

$$4HSi(OEt)_3 \longrightarrow SiH_4 + 3Si(OEt)_4$$

The interchange of alkoxy groups between alkoxysilanes[3] and the disproportionation of various alkenylalkoxysilanes[4] have been reported in the presence of alkaline catalysts. Bailey disclosed that disproportionation took place when phenylalkoxysilanes were heated with sodium alkoxides,[5] although alkylalkoxysilanes were unaffected by similar conditions. Redistribution of phenyl groups also has been observed by Beck[6] and others in rearrangements of phenylsiloxanes at high temperatures.

Our work has confirmed the disproportionation of phenylalkoxysilanes disclosed by Bailey. Specifically it was shown that phenyltrimethoxysilane and phenylmethyldimethoxysilane form tetramethoxysilane and methyltrimethoxysilane, respectively, when heated in the presence of catalytic amounts of sodium. The other products of these reactions are materials containing more than one phenyl group attached to silicon:

$$C_6H_5Si(OMe)_3 \longrightarrow (MeO)_4Si + C_6H_5Si(OMe)_3 + (C_6H_5)_2Si(OMe)_2 + (C_6H_5)_3SiOMe + (C_6H_5)_4Si$$

$$(C_6H_5)MeSi(OMe)_2 \longrightarrow MeSi(OMe)_3 + (C_6H_5)_2MeSiOMe + (C_6H_5)_3SiMe$$

At the temperatures employed in the latter experiments (200°), it is significant that the methyl group did not take part in the disproportionation. The actual catalyst in these systems very likely is the hydroxide or methoxide ion generated by reaction of sodium with moisture or free methanol which are certainly present in these systems.

The exchange of phenyl and alkoxy groups attached to silicon was extended to a procedure which could be a useful method of preparing any number of phenyl-containing alkoxysilanes

$$MeSi(OMe)_3 + (C_6H_5)_x\,Si(OMe)_{4-x} \longrightarrow Si(OMe)_4 + (C_6H_5)_y\,MeSi(OMe)_{3-y}$$
$$x = 1, 2;\ y = 0, 1, 2, 3, \ldots$$

These reactions are typical redistribution reactions under which conditions the methyl group does not participate, while the phenyl and methoxy groups are distributed in all possible combinations

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(1) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4815 (1959).

(2) C. Friedel and A. Ladenburg, *Ann.*, **143**, 124 (1867).

(3) D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, **68**, 77 (1946).

(4) (a) D. L. Bailey and A. N. Pines, *Ind. Eng. Chem.*, **46**, 2363 (1954); (b) A. N. Pines and R. E. Godlewski, U. S. Patent 2,851,474.

(5) D. L. Bailey, U. S. Patent 2,723,983; 2,723,985.

(6) E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter and A. J. Barry, *J. Am. Chem. Soc.*, **81**, 1256 (1959).