Acknowledgment.—We are greatly indebted to Mr. Oscar Blum, Mr. R. L. Ehrenfeld, and Dr. F. H. Winslow for permission to quote from their experimental work and to Miss Pearl Foster, Dr. Frank McKenna, Mr. J. M. Phelan, and Mrs. Rebecca Teston for analytical determinations.

Summary

Hexafluorobutadiene has been shown to be a highly reactive compound resembling in general butadiene rather than the relatively inert hexachlorobutadiene.

The thermal reactions of hexafluorobutadiene were investigated over the temperature range 150 to 180° and hexafluorocyclobutene, dimers, which were formed in largest amount, and trimers isolated as the principal products.

Hexafluorobutadiene dimer and trimer fractions were shown to be mixtures of isomers. On heating, the dimer was partially converted into a remarkable lower-boiling saturated and highly stable isomer for which a fused tricyclic structure was proposed. Hexafluorobutadiene trimer polymerized slowly on heating. Both dimer and trimer were partially depolymerized by passing through a hot tube.

Ithaca, N. Y.

Received August 21, 1948

[Contribution from the Laboratory of Experimental Therapeutics, U. S. Public Health Service, and Johns Hopkins School of Hygiene and Public Health]

Disproportionation of Aromatic Stiboso Compounds. I. Mechanism[1]

By H. H. Jaffe[2] and G. O. Doak[2]

Stibosobenzene and its derivatives are known to disproportionate in the solid state at moderately elevated temperatures according to the equation[3]

$$4ArSbO \longrightarrow (Ar_2Sb)_2O + Sb_2O_3$$

In order to determine the mechanism of this reaction and possibly to elucidate the effect of structure on the stability of the carbon–antimony bond we have chosen to investigate the rate of the above reaction. The present paper is concerned with stibosobenzene alone: the effect of substitution will be presented in a later paper.

Experimental

Benzenestibonic acid, prepared by a method described previously,[4] was reduced in concentrated hydrochloric acid and ethyl alcohol with sulfur dioxide in the presence of a trace of hydriodic acid. The resulting solution of phenyldichlorostibine was hydrolyzed by dilute aqueous ammonia or sodium hydroxide.[3] The precipitated stibosobenzene was washed with 10 to 12 liters of water, alcohol and ether, and dried *in vacuo*.

Stibosobenzene, prepared in this manner, was obtained as an amorphous colorless solid, soluble in formic and acetic acids, but insoluble in other common organic solvents and in water. So far it has not been possible to prepare it in a crystalline state. The compound does not possess a well-defined melting point, but sinters at approximately 154°, although this temperature varies somewhat with the rate of heating. The molecular weight is unknown. Cryoscopic measurements in formic and acetic acids gave anomalously large depressions, probably due to reaction with the solvents. By analogy with antimony trioxide which exists in a bimolecular and a polymolecular form,[5] and with aromatic arsenoso compounds, which have molecular weights four times the formula weight,[6] stibosobenzene is probably not monomolecular.

In preliminary experiments it was demonstrated that the disproportionation of stibosobenzene at 100° yielded bis-(diphenylantimony)-oxide in quantitative yield. The product was identified by melting point and analysis. In an atmosphere of nitrogen no side reaction could be detected. It was further shown that extraction of a mixture of stibosobenzene, antimony trioxide and bis-(diphenylantimony)-oxide with five portions of ether (40 ml. each) permitted quantitative recovery of the bis-(diphenylantimony)-oxide, without contamination with stibosobenzene or antimony trioxide.

To determine the rate of disproportionation, samples of stibosobenzene (0.25 to 0.75 g.) were permitted to rearrange in large test-tubes in an atmosphere of nitrogen in a constant temperature bath maintained at fixed temperatures between 75 and 100°. Samples were withdrawn at accurately measured intervals, chilled in ice and extracted with ether. The extracts were evaporated *in vacuo* at room temperature and dried to constant weight. The bis-(diphenylantimony)-oxide was weighed and analyzed and the fraction of the original material that had rearranged was obtained from these data. The rate constants, k_2, were calculated from equation (1) below by the method of least squares using from 6 to 14 experimental points.

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(1) Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September 17, 1947.

(2) Present address: Syphilis Experimental Laboratory, School of Public Health, University of North Carolina, Chapel Hill, North Carolina.

(3) H. Schmidt, *Ann.*, **421**, 174 (1920).

(4) G. O. Doak and H. G. Steinman, This Journal, **68**, 1987 (1946).

(5) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945, p. 416.

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Results and Discussion

Kinetics.—The rearranged fraction $(1 - x)$ plotted against time (t) resulted in an S-shaped curve. This could be reduced to a linear relationship by plotting $\ln(1/x - 1)$ against t (except for the first portion of the curve) (Figs. 1a and b), corresponding to a rate law

$$-dx/dt = k_2(x)(1 - x) \qquad (1)$$

or in the integrated form

$$\ln\left(\frac{1 - x}{x}\right) = k_2(t - t_{1/2}) \qquad (1a)$$

where $t_{1/2}$ is the time required for one half of the original material to rearrange. The early portion of the curve deviated from the expected straight line in different directions depending on whether sodium hydroxide or ammonia was used in the synthesis. An explanation of this phenomenon will be suggested below.

The rate constants determined from equation (1) in a series of experiments using a single preparation of stibosobenzene were constant within the limits of experimental error (Table I). The constants obtained with different preparations varied over a wide range (Table II). In spite of this variation, the same rate law was found to apply in more than fifty experiments with eleven separate preparations.

TABLE I

THE RATE OF DISPROPORTIONATION OF A SINGLE PREPARATION OF STIBOSOBENZENE AT 78°

10^4k_2 sec.$^{-1}$	Standard error
3.11	0.20
3.16	.20
2.96	.20

TABLE II

THE RATE OF DISPROPORTIONATION OF VARIOUS PREPARATIONS OF STIBOSOBENZENE AT 78°

10^4k_2 sec.$^{-1}$	Standard error	10^4k^2 sec.$^{-1}$	Standard error
a. Hydrolyzed with Aqueous Ammonia		b. Hydrolyzed with Sodium Hydroxide	
4.73	0.29	0.514	0.15
3.08	.09	.651	.059
1.24	.27	.254	.011
3.52	.17	1.44	.04
5.21	.11	2.06	.09
4.63	.14		

The variation of the rate constants in different preparations is probably due to small amounts of impurities which could not be removed since stibosobenzene could not be purified. Tables III and IV show the effect of the addition of various substances to the rate of the reaction. It is seen that bases and bis-(diphenylantimony)-oxide are effective catalysts. The effect of hydrogen chloride and other strong acids could not be investigated because stibosobenzene reacts with acids to form ether soluble compounds.

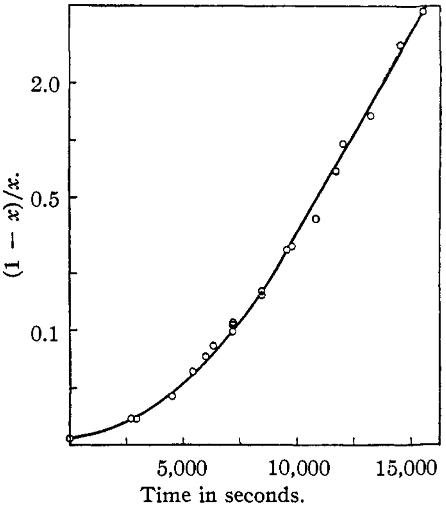


Fig. 1a.—The disproportionation of stibosobenzene at 78°: preparations hydrolyzed with aqueous ammonia.

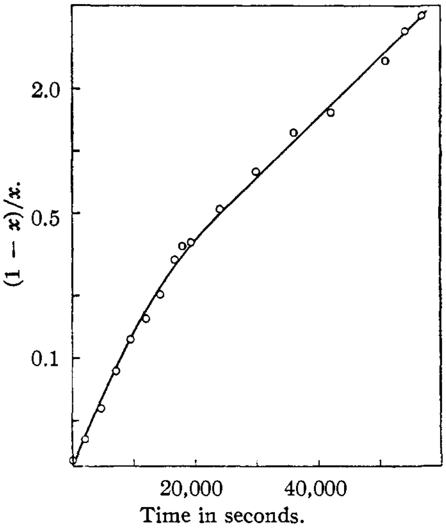


Fig. 1b.—The disproportionation of stibosobenzene at 78°: preparations hydrolyzed by sodium hydroxide.

The rate constant of one preparation of stibosobenzene was determined at three temperatures (Table V). The plot of $\ln k_2$ against $1/T$ (Fig. 2) permits calculation of the apparent energy of activation, E, which was 23.5 ± 1.5 kcal./mole.

TABLE III

THE EFFECT OF VARIOUS SUBSTANCES ON THE RATE OF DISPROPORTIONATION OF STIBOSOBENZENE AT 78°

Nature of substance	Amount: weight fraction of stibosobenzene	10^4k_2 sec.$^{-1}$	$10^4k_2(0)^a$ sec.$^{-1}$
$C_6H_5SbO_3H_2$	0.1	4.49	4.69
Powdered pyrex	.1	4.56	4.69
NH_3	.1 atm.	3.73	3.41

[a] Rate constant for same preparation of stibosobenzene without catalyst.

Mechanism.—From the experimental data several possible mechanisms for the reaction

TABLE IV

THE EFFECT OF VARIOUS SUBSTANCES ON THE RATE OF DISPROPORTIONATION OF STIBOSOBENZENE

Substance added	Amount: weight fraction of stibosobenzene	$(1 - x)_t$[a]	$(1 - x)_t$[b]
Vacuum	..	0.358	0.367
Sb_2O_3	0.1	.466	.492
Zn dust	.2	.367	.367
Na_2SO_3	.02	.369	.367
d	.1	.360	.367
CuCl	.02	.365	.367
Succinic acid	.1	.500	.492
$NaOAc \cdot 3H_2O$	.1	.774	.492
Na_2CO_3	.1	.522	.492
$[(C_6H_5)_2Sb]_2O$	.2	.417	.101
NaOH	.75	.215	.127
C_5H_5N	.2	.940	.367
NH_3	*c*	.645	.367

[a] Fraction rearranged after *t* min. at 78°. [b] Fraction of stibosobenzene without added catalyst rearranged after same time. [c] Under partial pressure of NH_3. [d] Mixture of equal parts of KBr, KCl, KI and $(NH_4)_2SO_4$.

TABLE V

THE EFFECT OF TEMPERATURE ON THE RATE OF DISPROPORTIONATION OF STIBOSOBENZENE

T, °K.	10^4k_2, sec.$^{-1}$	Standard error
350.6	5.21	0.11
362.1	12.8	1.0
373.2	33.4	1.5

can be suggested. The simplest interpretation of rate law (1) is a bimolecular, autocatalytic reaction. However no plausible reaction between stibosobenzene and bis-(diphenylantimony)-oxide to form more of the latter product can be written. The fact that most of the effective catalysts for the reaction are liquids at the experimental temperatures (pyridine, sodium acetate and bis-(diphenylantimony)-oxide) suggests that the reaction occurs in solution, the supposed catalyst functioning by virtue of its solvent power for stibosobenzene. The catalysis by dry ammonia and sodium hydroxide is an argument against such a mechanism. Further, the kinetics of such a reaction would be expected to be first order with respect to the solvent, to give a break when the solvent is no longer saturated with stibosobenzene, and thereafter to be first order with respect to stibosobenzene. No such break has been observed in following the reaction to completion.[7]

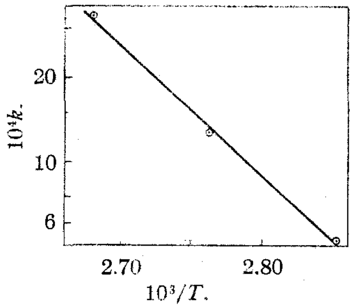


Fig. 2.—The effect of temperature on the rate of disproportionation of stibosobenzene.

Reactions occurring in the solid phase have usually been interpreted as interface reactions,[8] which follow the rate law

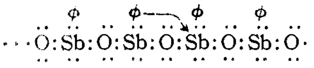
$$-\frac{dx}{dt} = \frac{d(1 - x)}{dt} = k(1 - x)^{2/3}$$

in the early portion of the reaction, and later approach the rate law

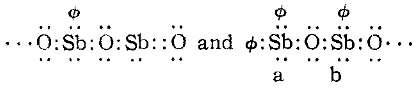
$$-dx/dt = k'x^{2/3}$$

The rate of disproportionation of stibosobenzene did not conform with these kinetics. Also as an interface reaction catalysis by both products would be expected, while it was shown (Table IV) that antimony trioxide was not a catalyst, although bis-(diphenylantimony)-oxide was. Further the reaction obeyed the same rate law whether the catalytic product, the bis-(diarylantimony)-oxide, was liquid at experimental temperatures (stibosobenzene), or solid (the *p*-chloro and *p*-methyl derivatives).

Another possible mechanism, which seems to afford the best interpretation of the experimental facts, is a chain reaction; the initiating step of which is the transfer of a phenyl group (*ϕ*) from one antimony atom to an adjacent one

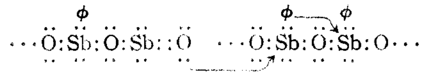


followed by splitting at the oxygen atom to yield fragments I and II.

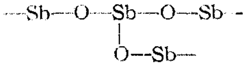


I II

The fragment I then attacks an adjacent antimony atom of stibosobenzene:



causing the shift of a phenyl group, thus propagating the chain, and forming the



grouping characteristic of antimony trioxide.[5]

Resonance with two phenyl groups lowers the electron density on antimony atom a in fragment II, compared with the antimony atoms in stibosobenzene. By an inductive effect the electron

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[7] The disproportionations of the *p*-Cl- and *p*-CH_3- derivatives of stibosobenzene (to be reported in a later paper) obey the same rate law, although the corresponding bis-(diarylantimony)-oxides are solid at the experimental temperature. This is a further argument against the above mechanism.

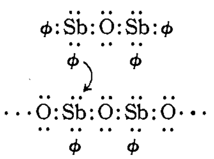
[8] *Cf.* G. M. Schwab, H. S. Taylor and R. Spence, "Catalysis," D. Van Nostrand Company, New York, N. Y., 1937, p. 324 ff.

density on antimony atom b is also lowered. This makes it less likely for this atom to lose a phenyl group than to gain one, thus forming bis-(diphenylantimony)-oxide.

The chain breaking reaction may be the recombination of a phenyl group with an antimony atom of fragment I, or the attack of the oxygen atom of fragment I on an antimony atom of another such fragment, or both.

The proposed mechanism considers the shift of a phenyl group as the first step in the reaction. It is not known at the present time whether this phenyl group shifts with or without its electron pair, or with only one electron. The formation of fragments I and II would result in any case.

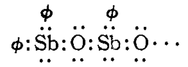
The autocatalysis by the product, bis-(diphenylantimony)-oxide, may be interpreted in terms of the following mechanism. A phenyl group migrates from a molecule of bis-(diphenylantimony)-oxide to an adjacent one of stibosobenzene.



$$\phi:\ddot{\underset{..}{Sb}}:\ddot{\underset{..}{O}}:\ddot{\underset{..}{Sb}}:\phi$$

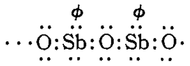
$$\cdots\ddot{\underset{..}{O}}:\ddot{\underset{..}{Sb}}:\ddot{\underset{..}{O}}:\ddot{\underset{..}{Sb}}:\ddot{\underset{..}{O}}\cdots$$

followed by a break at the antimony–oxygen bond. This process results in fragments II, III and IV.



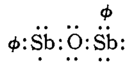
$$\phi:\overset{\phi}{Sb}:\ddot{\underset{..}{O}}:\overset{\phi}{Sb}:\ddot{\underset{..}{O}}\cdots$$

II



$$\cdots\ddot{\underset{..}{O}}:\overset{\phi}{Sb}:\ddot{\underset{..}{O}}:\overset{\phi}{Sb}:\ddot{\underset{..}{O}}\cdot$$

III



$$\phi:\ddot{\underset{..}{Sb}}:\ddot{\underset{..}{O}}:\overset{\phi}{Sb}:$$

IV

Fragment III has a reactive oxygen atom which can propagate the chain in the same manner as fragment I above, while fragment IV may act as a chain breaker. The reaction according to the above mechanisms would be expected to obey the rate law

$$-\mathrm{d}x/\mathrm{d}t = k'x[k_1'x + k_2'(1 - x)] \qquad (2)$$

where k' is the resultant rate constant of the chain propagating and chain breaking reactions, and k_1' and k_2' are the rate constants of the chain initiating steps (the thermal dissociations of stibosobenzene and bis-(diphenylantimony)-oxide respectively). Using $k_1 = k'k_1'$ and $k_2 = k'k_2'$ equation (2) can be written

$$-\mathrm{d}x/\mathrm{d}t = k_1x^2 + k_2x(1 - x) \qquad (2a)$$

If $k_2 \gg k_1$ equation (2a) will reduce to equation (1) except when $(1 - x) \ll x$, *i. e.*, for the first portion of the reaction.

The rate curves for all the preparations of stibosobenzene hydrolyzed with aqueous ammonia followed equation (2a) throughout (Fig. 1a). Equation (2a) can be integrated to give

$$\ln (k_2/x - k_2 + k_1) = k_2(t - C) \qquad (2b)$$

It is easily seen that this reduces to (1a) if $k_2 \gg k_1$, and that as a good approximation

$$C = t_{1/2} - (\ln k_2)/k_2$$

Substitution of this value for C and solving for k_1 leads to the expression

$$k_1 = k_2 \left[1 - \frac{1}{x} + e^{-k_2(t_{1/2} - t)}\right] \qquad (2c)$$

which permits calculation of k_1. Six experimental points (Fig. 1a) give $k_1 = 0.102 \pm 0.008 \times 10^{-4}$ sec^{-1}. For the same preparation of stibosobenzene k_2 was found to be $4.68 \pm 0.14 \times 10^{-4}$ sec.$^{-1}$, and therefore $k_1 = 0.02\ k_2$, which bears out the assumption that $k_2 \gg k_1$. Since all experimental curves for stibosobenzene preparations hydrolyzed by ammonia gave the same characteristic curvature it seems probable that the ratio k_1/k_2 remains approximately constant regardless of the amount of catalyst present.

The early portion of the rate curves obtained with preparations hydrolyzed with sodium hydroxide showed a rapid initial rate, an effect opposite to that obtained with preparations hydrolyzed with aqueous ammonia (Fig. 1b). In spite of this the rate constants k_2 calculated from equation (1) from the main portion of the curve, but neglecting the early portion, were slower than those from the products hydrolyzed with ammonia (Table II). This may be explained by the assumption that sodium hydroxide molecules, while actually catalyzing the reaction more than ammonia molecules, cannot freely diffuse through the reaction mixture, and are thus effectively prevented from catalyzing more than the initial phase of the reaction. It might be possible to remove all traces of catalyst by partially rearranging samples of stibosobenzene, and extracting the bis-(diphenylantimony)-oxide together with the entrapped catalyst. The rate constant of the resulting product might then approximate that of pure stibosobenzene, free from catalyst.

To test this postulate large samples of stibosobenzene (10–15 g.) prepared by hydrolysis with sodium hydroxide were permitted to rearrange partially, extracted with ether and dried. The amount of stibosobenzene in the resulting mixture was determined by antimony analysis. The rate of disproportionation of the stibosobenzene in these mixtures containing antimony trioxide was then determined in the usual manner. A definite reduction of the rate constant was observed, which was not due to negative catalysis by antimony trioxide, since increasing amounts of the latter did not further retard the reaction. Nevertheless, the rate constants obtained from two different mixtures prepared in this manner were not in agreement (Table VI). It appears that the deter-

TABLE VI

THE RATE OF DISPROPORTIONATION OF STIBOSOBENZENE AT 78° AFTER PARTIAL DISPROPORTIONATION

Original material		Resulting material	
10^4k_2, sec.$^{-1}$	Standard error	$k_2 \times 10^4$ sec.$^{-1}$	Standard error
2.06	0.09	0.341	0.015
0.254	.011	.155	.008

mination of the true rate constant for the disproportionation of stibosobenzene awaits the preparation of pure samples of the compound.

Acknowledgment.—The authors wish to acknowledge the assistance by Claire T. Brooks and Joseph J. Holechek throughout the course of this work. The interest of Harry Eagle is also gratefully acknowledged.

Summary

1. The kinetics of the disproportionation of stibosobenzene were determined. From 20 to 100% completion the reaction was shown to obey a rate law: $-dx/dt = k_2x(1 - x)$, where x is the fraction of stibosobenzene remaining at time t.

2. Preparations of stibosobenzene hydrolyzed with aqueous ammonia obeyed a rate law: $-dx/dt = k_1x^2 + k_2x(1 - x)$ over the entire course of the reaction, and the ratio k_1/k_2 was found to be 0.02.

3. The reaction was shown to be catalyzed by the product, bis-(diphenylantimony)-oxide, and by bases such as sodium hydroxide, ammonia and pyridine.

4. Rate constants were reproducible for each preparation, but varied widely with different preparations, an effect which is probably due to traces of impurities.

5. The apparent energy of activation was found to be 23.5 kcal./mole.

6. As mechanism of the reaction a chain reaction is proposed which is initiated by the thermal dissociation of phenyl groups from stibosobenzene and bis-(diphenylantimony)-oxide.

RECEIVED[9] SEPTEMBER 29, 1948

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[9] Original manuscript received May 5, 1948.

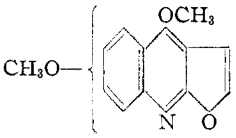
[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, UNIVERSITY OF WISCONSIN, AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALCUTTA, INDIA]

On the Constitution of the Active Principles Isolated from the Matured Bark of *Aegle marmelos*, Correâ

BY ASIMA CHATTERJEE AND SUDHANGSU SEKHAR MITRA

The tree *Aegle marmelos*, Correâ (*Rutaceae*) commonly known as Bael, is indigeneous to India and found wild all over the Sub-Himalayan forests, in Central and South India. Its wood is yellowish-white with a strong aromatic scent. It is reputed to be a valuable Ayurvedic medicine for dysentery and various intestinal complaints. The bark as well as the fruits are used for this purpose. An examination of the fruits by various workers has revealed the occurrence of a coumarin[1] termed "marmelosin" which is identical with imperatorin,[2] a furocoumarin isolated from *Imperatoria ostruthium*[3] and *Angelica archangelica*.[4] The isolation of three crystalline constituents of the *Aegle marmelos* bark was described earlier.[5] We wish to report that one is an alkaloid identical[6] with γ-fagarine[7]; the second compound is marmesin, a coumarin which has not been isolated so far from other natural sources; and the third compound is umbelliferone.

Hydrochloric acid washing of ethereal bark extracts yielded a basic portion from which an alkaloid, m. p. 142.5–143°, was separated in 0.3% yield, which has been shown by Chakravarty[6] to be identical with γ-fagarine[7] (I).



I

The remaining ether extract upon concentration and standing in the refrigerator deposited crystals of marmesin, m. p. 189.5°, in a 0.6% yield. The mother liquor, after alkali washings and steam distillation, deposited umbelliferone m. p. 230° (yield, 0.06%).

The molecular formula of marmesin appeared to be $C_{14}H_{14}O_4$ which was confirmed by Rast's method and also by titration. Marmesin is optically active, $[\alpha]^{34}D$ +26.8° (in chloroform). This compound does not contain methoxy or methylenedioxy groups. It yields a monoacetyl derivative and readily undergoes dehydration producing anhydromarmesin. These facts indicate the presence of an hydroxyl group. Since the compound does not react with ferric chloride or diazomethane, it must contain an alcoholic group. Marmesin is neutral to litmus and is insoluble in aqueous alkali but readily dissolves in alcoholic alkali with a stable yellow color. This solution precipitated, on acidification, the original substance indicating a lactone structure. Marmesin dissolves in concentrated sulfuric acid with a yellow color and a deep violet fluorescence. When refluxed with aqueous alkali and a little mercuric oxide, marmesin passed into solution and, on acidification with hydrochloric acid, yielded an acid which did not undergo ring closure to give the

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[1] B. B. L. Dikshit and S. Dutt, *J. Indian Chem. Soc.*, **7,** 759 (1930); **9,** 271 (1932).

[2] E. Späth, P. K. Bose, W. Grüber and N. C. Guha, *Ber.*, **70,** 1021 (1937).

[3] E. Späth and H. Holsen, *ibid.*, **66,** 1137 (1933).

[4] E. Späth and F. Vierhapper, *ibid.*, **70,** 248 (1937).

[5] A. Chatterjee (née Mookerjee), *Current Science*, **12,** 209 (1943).

[6] K. K. Chakravarty, *J. Indian Chem. Soc.*, **21,** 401 (1944).

[7] V. Deulofeu, R. Labriola and J. Langhe, THIS JOURNAL, **64,** 2326 (1942).