

IX, beautiful sparse clusters of colorless triangular prisms from acetone-methanol, m. p. 220–221° (lit.^{13a} m. p. 214°). Another sample of IX (from reduction of VII) exhibited dimorphism; on seeding a supercooled solution of the material in acetone-methanol, colorless needles were rapidly deposited which changed into massive granules, the interconversion being complete in about three hours at 0°. These granules melted at 219.6–220.2°, resolidified on withdrawing from the bath, then melted at 226°; a sample mixed with authentic IX showed the same behavior.

Anal. Calcd. for $C_9H_{13}BrN$: C, 46.16; H, 8.71; N, 6.73. Found: C, 45.75; H, 8.77; N, 6.39.

The above salts gave the corresponding picrate, bright yellow-orange dendrites from ethanol, m. p. 116.5–117.1°.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.40; H, 5.75; N, 15.50.

The halides with excess of aqueous sodium picrate gave a picrate-sodium picrate double salt,²⁰ fine yellow needles from ethanol, m. p. 164.4–164.7° (prior sintering).

Anal. Calcd. for $C_{14}H_{20}N_4O_7 \cdot C_6H_5N_3NaO_7 \cdot 0.5H_2O$: C,

38.97; H, 3.76; N, 15.91; Na, 3.73. Found: C, 38.83; H, 4.04; N, 16.26; Na, 3.39.

Catalytic reduction¹² of VII gave in good yield IX (mixed m. p. with authentic IX) which was converted to the picrate (mixed m. p.). A very small yield of IX (isolated as the picrate-sodium picrate double salt, mixed m. p. and analysis) resulted from the reduction¹² of crude V using a palladium-on-Norit catalyst; trimethylamine hydrobromide constituted the major reaction product.

Summary

The Ziegler bromination of methylenecyclobutane has been studied. The major bromination product is the olefin dibromide and under the best conditions found (in benzene and with added peroxide) the yield of allylic bromides is 14%.

The allylic bromides were investigated by conversion to the allylic trimethylammonium bromides, the structures of which were established.

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[CONTRIBUTION FROM THE COATES LABORATORIES OF LOUISIANA STATE UNIVERSITY]

Analysis of the Vibrations of Benzene Derivatives. I. The Class A_1 Carbon Vibrations of Toluene

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The assignment of experimentally observed vibrational frequencies of aromatic molecules to definite modes of vibration has encountered difficulties, chief of which has been the large number of vibrations belonging to each symmetry class. Only for the highly symmetrical benzene molecule has it been possible to make assignments with confidence.

For toluene, the assignments have been more speculative. The polarization measurements in the Raman spectrum made by Cabannes and Rousset³ and by Cleveland⁴ have been of importance in identifying the totally symmetric vibrational frequencies. However, the number of observed polarized lines is less than the theoretical number of totally symmetric vibrations, even if toluene is assigned C_{2v} symmetry. Teets and Andrews⁵ constructed a mechanical model of toluene, and found certain correlations between its vibrational frequencies and those observed in the Raman spectrum of toluene. Pitzer and Scott,⁶ reasoning by analogy with benzene, assigned a frequency and vibrational form to each of the fundamental vibrations of the toluene molecule. However, except for the 1003 cm^{-1} frequency, they did not analyze the changes that occur in the vibrational forms on going from benzene to toluene.

Ginsburg, Robertson and Matsen⁷ have analyzed the near-ultraviolet absorption spectrum of toluene vapor and made a considerable number of frequency assignments.

Recently, the authors⁸ have developed an interpretation of the ultraviolet absorption spectrum of toluene which differs from that of Ginsburg, Robertson and Matsen in that the 623 cm^{-1} frequency (in the ground state) is assigned to Class A_1 instead of Class B_1 . Furthermore, the authors have proposed certain approximate vibrational forms for the Class A_1 carbon vibrations of toluene. These forms were based upon analogies with benzene and upon frequency changes taking place upon the substitution of deuterium for the various hydrogens of toluene. They differ in some cases from the forms assigned by Pitzer and Scott,⁶ and from the forms observed in the mechanical model.⁵

In an attempt to settle these differences in the assignment of the frequencies and modes of vibration of toluene, the mathematical analysis presented in this article was made.

Calculations

In order to simplify the mathematical analysis, the carbon and hydrogen vibrations are treated as distinct uncoupled sets. This follows a previous qualitative treatment of the benzene vibrations.⁹ For the purpose of the calculation of the carbon vibrations, it is assumed that each hydrogen is

(7) Ginsburg, Robertson and Matsen, *J. Chem. Phys.*, **14**, 511 (1946).

(8) Choppin and Smith, *THIS JOURNAL*, **70**, 577 (1948).

(9) Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson and Wilson, *J. Chem. Soc.*, 971 (1936).

(1) American Chemical Society Post-doctoral Research Fellow at Louisiana State University.

(2) The authors are indebted to Newton Grant for checking some of the calculations.

(3) Cabannes and Rousset, *Ann. phys.*, **19**, 229 (1933).

(4) Cleveland, *J. Chem. Phys.*, **13**, 101 (1945).

(5) Teets and Andrews, *J. Chem. Phys.*, **3**, 175 (1935).

(6) Pitzer and Scott, *THIS JOURNAL*, **68**, 803 (1943).

TABLE I
NORMAL COÖRDINATES FOR THE CLASS A₁ CARBON VIBRATIONS OF TOLUENE

Comparing with Figure 1, the upward direction of the vertical component and the outward direction of the horizontal component are given positive signs.

Normal coördinate	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5	ξ_6
Calcd. freq. (cm. ⁻¹)	497	779	965	1156	1380	1704
Me-group motion	1.00	1.00	0.12	-0.61	0.36	-0.21
C-1 motion	0.52	-0.20	-0.10	1.00	-1.00	1.00
C-2 motion (total)	0.36	0.80	0.95	0.90	0.22	1.06
C-2 (horiz. comp.)	-0.31	0.74	-0.78	-0.78	-0.22	0.40
C-2 (vert. comp.)	-0.17	-0.30	-0.56	0.44	0.02	-0.99
Angle C-2 with horiz.	29°	22°	36°	29°	4°	68°
C-3 motion (total)	0.41	1.11	0.06	1.26	0.57	0.90
C-3 (horiz. comp.)	-0.28	1.00	0.04	1.25	0.27	0.20
C-3 (vert. comp.)	-0.30	-0.49	0.04	-0.22	0.50	0.88
Angle C-3 with horiz.	47°	26°	40°	10°	60°	77°
C-4 motion	-0.70	0.61	1.00	-0.66	-0.52	-0.46
% of V due to K_1	23	26	1	16	27	6
% of V due to K_2	8	37	51	48	63	82
% of V due to $K\alpha$	69	37	48	36	10	12

condensed into the nucleus of the carbon atom to which it is attached, forming a "molecule" containing seven mass-points. The methyl group has a relative mass of 15, the carbon in position one a mass of 12, and each of the other carbons a mass of 13. The "molecule" belongs to point-group C_{2v}. It has 15 normal vibrations, six belonging to Class A₁ (totally symmetric), one belonging to Class A₂ (symmetric only with respect to the two-fold axis), five belonging to Class B₁ (symmetric only with respect to the molecular plane), and three belonging to Class B₂ (symmetric only with respect to the plane of symmetry perpendicular to the molecular plane). When the secular equation is expressed in terms of symmetry coördinates,¹⁰ it can be factored into four separate equations, one for each symmetry class. The Class A₁ vibrations may be set up in a sixth-order determinant. The calculations of this article use a valence-force potential system with the following force constants: 4.50×10^5 dynes per cm.,¹¹ valence-stretching constant for the single bond; 7.58×10^5 dynes per cm.,¹² valence-stretching constant for the aromatic bonds; 0.65×10^5 dynes per cm.,¹² force constant for the bending of the aromatic -C-C-C-angle in the plane of the ring. The single bond force constant was calculated by Stitt from an analysis of the ethane molecule. This particular value does not include interaction between the hydrogens of ethane. It was used since Pitzer and Scott⁶ found that the methyl group of toluene has essentially free rotation. The aromatic bond force constants were calculated by Lord and Andrews from the benzene molecule. The aromatic bond distances in toluene were assumed to be the same as in benzene; it is not necessary to use any actual values.

The six roots of the Class A₁ factor of the secular

equation are as follows: 497, 779, 965, 1156, 1380 and 1704 cm.⁻¹. The normal coördinates are given in Table I and in Fig. 1.

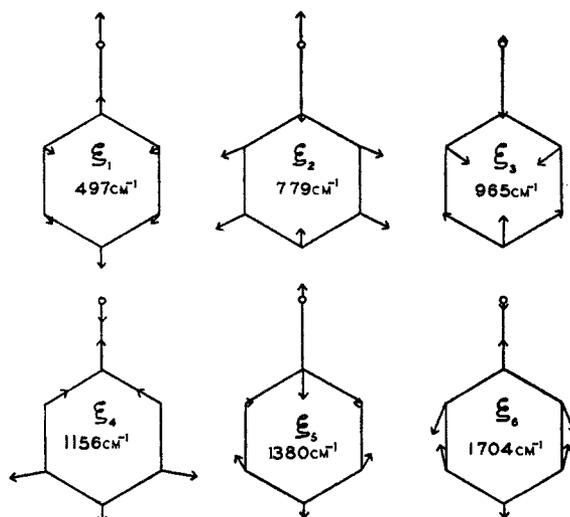


Fig. 1.—Calculated frequencies and normal coördinates for the Class A₁ carbon vibrations of toluene.

Discussion

Comparison with Spectral Frequencies.—Theoretically, all of the Class A₁ carbon vibrations should be active in the Raman spectrum (giving polarized lines) and in infrared and ultraviolet absorption. Possible correlations between calculated and observed frequencies of toluene are shown in Table II.

The frequency changes taking place when deuterium is placed on the toluene molecule⁸ are of value in checking the vibrational forms. If deuterium is placed upon a carbon atom which is vibrating with a large amplitude, there will be a greater decrease in frequency than would be the

(10) Howard and Wilson, *J. Chem. Phys.*, **2**, 630 (1934).

(11) Stitt, *ibid.*, **7**, 297 (1939).

(12) Lord and Andrews, *J. Phys. Chem.*, **41**, 149 (1937).

TABLE II
COMPARISON OF CALCULATED FREQUENCIES OF TOLUENE
WITH OBSERVED VALUES
Frequencies are given in cm.^{-1}

Calculated	Raman ^{13,14} (Pol.) ⁴	Ultraviolet ^{7,8}	Infrared ¹⁵
497	520 (0.44)	520	521
779	786 (0.03)	787	786
965	1003 (0.13)	1003	1003
	1029 (0.11)	..	1030
1156	1209 (0.29)	1210	1211
1380	1379 (0.46)	..	1379
			1460
			1497
1704	1736
			1802

case if the deuterium were placed upon a carbon atom vibrating with a small amplitude.

The calculated 497 cm.^{-1} frequency correlates with the polarized 520 cm.^{-1} Raman line. The frequency changes upon deuteration check with the calculated normal coordinate, ξ_1 , except for the meta carbon atom.

No calculated frequency lies near the observed 623 cm.^{-1} line. It must be concluded that this frequency *does not* correspond to a Class A_1 carbon vibration. This is in agreement with the observation that this line is depolarized in the Raman spectrum. It disagrees with the authors' previous assignment.⁸

The calculated 779 cm.^{-1} frequency correlates with the polarized 786 cm.^{-1} Raman line. The frequency changes upon deuteration check with the calculated form, ξ_2 , except for toluene-2-*d* in the ground state.

From Raman data alone, the calculated 965 cm.^{-1} frequency could belong to either the 1003 or the 1029 cm.^{-1} Raman line. However, the 1029 cm.^{-1} frequency was not observed in ultraviolet absorption. This gives rise to the assumption that the 1029 cm.^{-1} Raman line belongs to a Class A_1 hydrogen-bending vibration. This idea is supported by the observation of a line, which has been assigned to a Class A_1 hydrogen-bending vibration, at 1031.0 cm.^{-1} in the Raman spectrum of benzene-*d*.¹⁶ The observed 1003 cm.^{-1} line must correspond with the 965 cm.^{-1} calculated frequency (ξ_3). In the ground state, frequency changes upon deuteration check, with form ξ_3 in every case. This coordinate, where the motion is chiefly confined to the 2, 4 and 6 positions, strikingly confirms the form deduced by Pitzer and Scott⁶ from a consideration of the spectra of benzene and the methyl benzenes. In ultraviolet absorption, two strong frequencies were observed

(13) Howlett, *Can. J. Res.*, **5**, 472 (1931).

(14) Kohlrausch and Wittek, *Monatsh.*, **74**, 1 (1941).

(15) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Infrared Spectrograms. Serial Numbers 308 and 480, toluene (liquid), contributed by the U. S. Naval Research Laboratory, Washington, D. C.

(16) Bailey, Gordon, Hale, Herzfeld, Ingold and Poole, *J. Chem. Soc.*, 299 (1946).

in the excited state in this spectral region (933 and 966 cm.^{-1} for toluene). One possible explanation is that the hydrogen-bending vibration, observed at 1029 cm.^{-1} in the Raman spectrum, is coupled in with the carbon vibrations in the excited state, even though it does not appear in the ultraviolet absorption for the ground state. A more probable explanation lies in assigning one of these excited state lines to a carbon vibration of another symmetry class. It is to be noted that, for the excited state, the group of frequencies in the deuterated toluenes, beginning with 966 cm.^{-1} for toluene itself, check with the form of the normal coordinate ξ_3 .

The calculated 1156 cm.^{-1} frequency corresponds with the observed 1209 cm.^{-1} polarized Raman line. The observed frequencies of the deuterated toluenes are not in particularly good agreement with the form ξ_4 .

The calculated 1380 cm.^{-1} frequency is near the 1379 cm.^{-1} polarized Raman line. However, this frequency was not observed in ultraviolet absorption; it differs from other correlated frequencies in that the calculated value is not lower than the observed value. This makes its correlation questionable, especially since Pitzer and Scott⁶ correlated the 1379 cm.^{-1} Raman line with the symmetric hydrogen-bending motion within the methyl group. Cabannes and Rousset⁹ observed a polarized Raman line at 1483 cm.^{-1} and Pitzer and Scott⁶ assigned this line to a Class A_1 vibration. However, neither Howlett¹³ nor Kohlrausch and Wittek¹⁴ observed a Raman line at 1483 cm.^{-1} , raising doubt as to its actual existence. Several infrared bands have been observed in the region¹⁵; possibly one of them may correspond to the calculated form ξ_5 . Apparently, ξ_5 is not active in either the Raman spectrum or near-ultraviolet absorption.

The calculated 1704 cm.^{-1} frequency is far removed from the 1603 cm.^{-1} line which Pitzer and Scott⁶ assigned to a Class A_1 vibration, and no Raman lines have been observed near the calculated value. Possibly, one of the frequencies observed in the infrared may correspond to form ξ_6 . Apparently, ξ_6 is inactive in both the Raman and ultraviolet spectra.

Comparison with the Vibrations of Mechanical Models.—Teets and Andrews⁵ constructed a mechanical model of the toluene molecule and observed its vibrational forms and frequencies. Unfortunately for comparison with the calculated frequencies, they used the centric formula of benzene as the basis for their model. This resulted in relatively high frequencies for those vibrations involving bending of the ring.

Trenkler¹⁷ constructed mechanical models for mono-substituted benzene, using the resonating benzene formula as the basis for his model. One of the models had a mass distribution somewhat similar to that found in toluene. The actual form

(17) Trenkler, *Physik. Z.*, **37**, 338 (1936)

of the vibrations of these models has been given by Kohlrausch.¹⁸ The agreement between the calculated forms and frequencies and those observed in the model is not bad, except that Trenkler's form ω_3 has more motion in the meta carbon atoms than does form ξ_3 , and its frequency is completely out of line with both calculated and observed values.

Summary

The approximate vibrational forms and frequencies of the Class A₁ carbon vibrations of toluene have been calculated, using a simplified valence-force potential system and force constants from benzene and ethane. The calculated vibra-

(18) Kohlrausch, *Physik. Z.*, **37**, 58 (1936).

tions have been compared with spectral frequencies and with the vibrations of mechanical models. The results have been interpreted so as to indicate the following:

1. The observed 623 cm.⁻¹ frequency of toluene does not belong to a Class A₁ carbon vibration.
2. The 520, 786, 1003 and 1210 cm.⁻¹ observed frequencies of toluene belong to Class A₁ carbon vibrations.
3. The 1029 and 1379 cm.⁻¹ frequencies of toluene belong to symmetric hydrogen-bending vibrations.
4. Two of the Class A₁ carbon vibrations of toluene are not active in either the Raman or the near-ultraviolet absorption spectra.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Thiophosphorylethoxydichloride¹

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Inasmuch as thiophosphoryl trichloride has been stepwise fluorinated in this Laboratory⁴ to give thiophosphoryl chlorofluorides and trifluoride, it was of interest to study the effect of substituting an ethoxy group for a chlorine atom upon the fluorination reaction. Therefore, the fluorination of thiophosphorylethoxydichloride by the Swarts reaction was undertaken.

Experimental

Preparation and Purification of Thiophosphorylethoxydichloride.—The thiophosphorylethoxydichloride was prepared by a modification of the directions given by Pishchimuka⁵ from thiophosphoryl trichloride and dried, redistilled absolute ethyl alcohol. The thiophosphoryl trichloride was a C. P. (chemically pure) grade obtained from the Victor Chemical Company which was then fractionally distilled.

Two hundred grams of thiophosphoryl trichloride was placed in a three-necked flask fitted with a stirrer, drying tube and a separatory funnel containing 100 g. of absolute ethyl alcohol. The alcohol was added dropwise over a period of two to three hours, care being exercised that the temperature of the reactor did not exceed 10° thus reducing the yield. The crude thiophosphorylethoxydichloride was fractionated once under a pressure of 70 mm. and 4 times under a pressure of 25 mm. in a Raschig ring-packed electrically heated column to give a 70% yield of the purified product.

(1) From a thesis presented by Fred E. Kendall to the Graduate School of Western Reserve University, February, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy and based upon work done in connection with a research project sponsored by the Naval Research Laboratory, Office of Research and Inventions, U. S. Navy Department. Publication delayed for security reasons.

(2) Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

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(4) H. S. Booth and M. C. Cassidy, *THIS JOURNAL*, **62**, 2369-2372 (1940).

(5) P. S. Pishchimuka, *Ber.*, **41**, 3854-3859 (1908); *J. Russ. Phys. Chem. Soc.*, **44**, 1406-1554 (1912).

(6) E. Clemmensen, U. S. Patent 1,945,183, Jan. 30, 1934 (to Monsanto Chemical Co.).

Fluorination of Thiophosphorylethoxydichloride.—The method and apparatus used for the stepwise fluorination, using the Swarts reaction,⁷ was the same as that described elsewhere,^{8,9} except that, owing to the high boiling points of the products, an air-cooled condenser was substituted for the usual water-cooled condenser. In order to obtain the chlorofluoride, the fluorination products were removed with an automatic stopcock set to maintain a pressure of 20-30 mm. in the generator. The temperature of the generator must be at, or below, 50° to prevent decomposition of thiophosphorylethoxydichloride and thiophosphorylethoxychlorofluoride. In exploratory fluorination reactions, it was observed that simple addition of antimony trifluoride to thiophosphorylethoxydichloride in a flask, open to the atmosphere through a drying tube, produced about the same results providing the temperature of the reactor was kept below 50°. Little or no reaction was observed when the fluorination was attempted without antimony pentachloride as the catalyst.

Purification of Thiophosphorylethoxydifluoride.—The fluorination products were fractionally distilled in a modified Dufton column as described by Booth and Bozarth.¹⁰ The best coolant for the column head was water, cooled by ice and salt. Samples, from separate generations, were collected by distillation at two different operating pressures, namely, 60 and 100 mm., and found to be identical. The tailings in the still pot had such a low vapor pressure that their distillation in this type of fractionating column was not possible.

Purification of this compound was first attempted with the heated column used to purify the starting material. The distillation was attempted at atmospheric pressure with the receiver open to the atmosphere through a drying tube. However, a reaction of a volatile product with the atmosphere outside the drying tube was observed so this method of purification was abandoned.

Purification of Thiophosphorylethoxychlorofluoride.—The tailings of the above distillations were placed in the heated column used for the purification of thiophosphorylethoxydichloride and were fractionally distilled at pressures of 25 and 70 mm. These samples were found to be

(7) F. Swarts, *Acad. roy. Belg.*, **24**, 309 (1892).

(8) H. S. Booth and C. F. Swinehart, *THIS JOURNAL*, **54**, 4751-4753 (1932).

(9) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927-2934 (1939).

(10) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470-475 (1937).