Tetrahedron, 1958, Vol. 3, pp. 132–139. Pergamon Press Ltd., London

THE STRUCTURE OF LAGIDZE'S *CYCLO*BUTADIENE DERIVATIVES—I*

THE "$C_{14}H_{10}$ HYDROCARBON"

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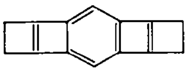
Abstract—The hydrocarbon resulting from the reaction of benzene with the diacetate of but-2-yne-1,4-diol in presence of aluminum chloride is shown to be 2-phenylnaphthalene, and not a benz*cyclo*butadiene derivative, as has been suggested.

AMONG the hydrocarbons of theoretical interest to the organic chemist, the unknown *cyclo*butadiene (I) is perhaps the simplest. Experiments directed towards the synthesis of compounds containing a simple *cyclo*butadiene system have so far all failed,[1,2,3,4,5] although a dimer of tetramethyl*cyclo*butadiene has apparently been prepared.[6,7]

I

Our interest in this field was occasioned by a report of Lagidze and Petrov,[8] stating that a hydrocarbon, $C_{14}H_{10}$ (m.p. 102°), prepared by reaction† of benzene, aluminum chloride and the diacetate of but-2-yne-1,4-diol probably possessed the structure of a benz*cyclo*butadiene derivative (II). Much of the data appeared to be in



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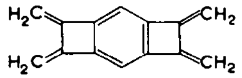

III

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[*] Adapted from the B.A. thesis of Harry W. Taber, Reed College, May 1957.

[†] In the description of this synthesis (cf. Lagidze and Petrov[8]) mention is made of two other products, namely 4-acetoxy-1-chlorobut-2-yne (in an unstated yield), and an acetophenone derivative (20 per cent). We have been unable to duplicate the formation of these products, and also the yield (12 per cent) claimed for the 102° hydrocarbon (see under "Experimental").

[1] D. R. Howton and E. R. Buchman, *J. Amer. Chem. Soc.* **78**, 4011 (1956); D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.* 4012.

[2] A. T. Blomquist and J. A. Verdol, *J. Amer. Chem. Soc.* **77**, 806 (1955).

[3] E. F. Jenney and J. D. Roberts, *J. Amer. Chem. Soc.* **78**, 2005 (1956); E. F. Silversmith and J. D. Roberts, *Ibid.* 4023.

[4] D. P. Craig, *J. Chem. Soc.* 3175 (1951); J. D. Roberts, A. Streitwieser and C. M. Regan, *J. Amer. Chem. Soc.* **74**, 4579 (1952).

[5] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.* 1969 (1956).

[6] I. V. Smirnov-Zamkov, N. A. Kostromina and G. A. Piskovitina, *Ukr. Khim. Zh.* **22**, 67 (1956): *Chem. Abstr.* **50**, 13761c (1956).

[7] R. Criegee and G. Louis, *Chem. Ber.* **90**, 417 (1957).

[8] R. M. Lagidze and A. D. Petrov, *Dokl. Akad. Nauk SSSR* **83**, 235 (1952); *Chem. Abstr.* **47**, 4321g (1953); *Chem. Zentr.* **125**, 1713 (1954): *Note added in proof*, 1 *March* 1958. LAGIDZE[8a] has recently published a retraction of his former views concerning the "$C_{14}H_{10}$ hydrocarbon" and his latest interpretations agree with those expressed here: cf. also a recent note by Maier.

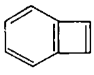
[8a] R. M. Lagidze, *Soobshchenya Akad. Nauk Gruzin. SSR* **19**, 279 (1957).

[8b] G. Maier, *Chem. Ber.* **90**, 2949 (1957).

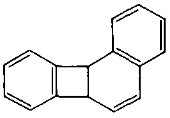
conflict with the reactions to be expected of a compound of this structure. Thus Lagidze and Petrov found that the hydrocarbon was stable to permanganate in the cold, that after ozonolysis it yielded formic and benzoic acids, and that on oxidation with chromic acid in acetic acid a yellow diketone, $C_{14}H_8O_2$, was formed.

It should be pointed out that, in their first paper, Lagidze and Petrov[8] assigned structure (III) to the $C_{14}H_{10}$ hydrocarbon, but, when it was found to be stable to permanganate, structure (II) was adopted. The possibility that the $C_{14}H_{10}$ hydrocarbon, m.p. 102°, was phenanthrene ($C_{14}H_{10}$, m.p. 101°) was abandoned, since a mixture of the two hydrocarbons showed a depression of the m.p. Compare also the monobromo substitution product of (II), m.p. 66°, and 9-bromophenanthrene, m.p. 63°.[9] It seemed possible also that the "yellow diketone" reported by Lagidze and Petrov[8] was a quinone (it gave a colored monoxime), but no compound corresponding to these properties derived from a $C_{14}H_{10}$ hydrocarbon has been reported in the literature.

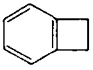
Recent work by Cava and Napier[10] on the synthesis and properties of benz*cyclo*butadiene (IV) has also raised doubts as to the correctness of formulation of the 102° hydrocarbon as (II). Thus although the saturated derivative (VI) proved stable, the compound (IV) appeared to dimerize readily via a Diels–Alder reaction to give (V) as the sole isolable material. It would therefore seem that the stability, if any, afforded to *cyclo*butadiene (I) by fusion with a benzene ring as in (IV) is not of practical significance as far as isolation of the compound is concerned. Thus were the "$C_{14}H_{10}$ hydrocarbon" to possess structure (II), Diels–Alder self-condensation would be expected, ending in polymerization.



IV

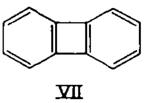


V



VI

Mention should also be made of a further related structure, namely that of diphenylene (VII).[11] This stable hydrocarbon bears only a passing formal resemblance to (I), since it would be expected that the apparent *cyclo*butadiene system present in structure (VII) would become incorporated into two essentially separate benzenoid systems.



VII

In the light of the foregoing, the latest structure (VIII) favored by the Russian workers[12] for the 102° hydrocarbon is perhaps more reasonable than the previous ones, since no benz*cyclo*butadiene system is present. Nevertheless, this structure is not without its objections, since oxidation would presumably lead to *o*-phthalic acid, not benzoic acid, and also isomerization to anthracene would be expected: none was

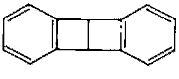
[9] *Beilsteins Handbuch, Hauptwerk* **5**, 671.

[10] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **78**, 500 (1956): *Ibid.* **79**, 1701, 1706 (1957).

[11] W. C. Lothrop, *J. Amer. Chem. Soc.* **63**, 1187 (1941).

[12] R. M. Lagidze, *Trud. Inst. Khim. Akad. Nauk Gruzin. SSR* **12**, 157 (1956); (in English translation by Associated Technical Services, P.O. Box 271, East Orange, New Jersey).

reported by the Russian workers (but see under "Experimental"). The conditions required for the synthesis of the 102° hydrocarbon—aluminum chloride at room temperature in benzene solution, followed by heating at 90° for 10 hr—would seem to facilitate aromatization of the above-mentioned kind.[13]



VIII

In view of these facts, it became necessary to re-investigate the structure of the "$C_{14}H_{10}$ hydrocarbon". The first four attempts yielded only viscous yellow oils, which did not crystallize in a refrigerator on standing. At this stage a written exchange with Professor Lagidze in Tbilisi assured us that the reaction was in fact feasible, and that he himself had recently checked the synthesis after we had informed him of our failures. At the second of three subsequent attempts we were successful in obtaining solid material, and the distilled reaction product solidified at once to a pale yellow mass of plates, which on crystallization from ethanol afforded colorless crystals, m.p. 102–103°. In agreement with the findings of the Russian workers, this substance gave a depression of m.p. when mixed with phenanthrene.

Evidently the conditions of the synthesis of the 102° hydrocarbon are quite critical: Lagidze himself informed us (in a personal communication, October 1956) that in some runs he had obtained viscous non-crystallizable oils, but he was unable to account for this erratic behavior.

The first indication that the molecular formula was not $C_{14}H_{10}$ resulted from the fact that the peak of highest *m/e* in the mass spectrum of the 102° hydrocarbon appeared at 204, suggesting $C_{16}H_{12}$ as a possible formula. The fact that the infrared spectrum of our 102° hydrocarbon matched that of 2-phenylnaphthalene provided the last clue to the identification of the substance. A sample prepared by the method of Elks and Hey[14] also melted at 102–103°, and showed no depression of m.p. on mixing. Further, the ultraviolet absorption of our hydrocarbon in methyl*cyclo*hexane showed λ_{max} at 249 and at 286 mμ. The published[15] spectrum in *cyclo*hexane also showed these maxima, as did a spectrum of the 102° hydrocarbon (in *n*-heptane) kindly furnished by Prof. Lagidze.

There can thus be no reasonable doubt that the 102° hydrocarbon is 2-phenylnaphthalene. The experimental data reported by the Russian workers can now be explained with reference to compounds most of which are already known (cf. Table 1).

Except for the molecular-weight data reported by Lagidze and Petrov, it is readily seen that the properties of the "$C_{14}H_{10}$ hydrocarbon" described by them correspond very closely with those of 2-phenylnaphthalene. Evidently too great an emphasis was placed by the Russian workers on combustion-analysis data (ambiguous in this case) and unfortunately the molecular-weight values they obtained were too low: the caus'

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[13] M. Turova-Pollak and M. Lukina, *J. Gen. Chem. USSR* **18**, 179 (1948); H. Pines, W. D. Huntsman and V. N. Ipatieff, *J. Amer. Chem. Soc.* **75**, 2315 (1953).

[14] J. Elks and D. H. Hey, *J. Chem. Soc.* 441 (1943).

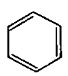
[15] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds.* John Wiley, New York (1951); R. A. Friedel, M. Orchin and L. Reggel, *J. Amer. Chem. Soc.* **70**, 200 (1948); W. M. Kutz, J. E. Nickels, J. J. McGovern and B. B. Carson, *Ibid.* **70**, 4029 (1948)

of this remains obscure, since Chattaway and Lewis[16] many years ago successfully determined the molecular weight of 2-phenylnaphthalene by the same method as that used by Lagidze and Petrov, i.e. a cryoscopic measurement in benzene.

TABLE 1.—COMPARISON OF DATA CONCERNING THE "$C_{14}H_{10}$ HYDROCARBON" AND 2-PHENYLNAPHTHALENE

Nature of data	Results of Lagidze and Petrov	Required on the basis of "$C_{14}H_{10}$"	For 2-phenyl-naphthalene[17]
Analysis of hydrocarbon	Found: C, 94·34 94·10, 94·21; H, 5·78, 5·78, 5·77	C, 94·34 H, 5·66	C, 94·08 H, 5·92
Molecular weight of hydrocarbon	188 ± 10 (X-ray) 177–184 (cryoscopic)	178	198 (cryoscopic[16]). Found: 204 (mass-spectrometer[18])
Monobromo compound	m.p. 65°		m.p. 66°
Mononitro compound	m.p. 129°, yellow crystals. Found: N, 5·84	Calcd. for $C_{14}H_9O_2N$: N, 6·27	m.p. 127° yellow needles. Calcd. for $C_{16}H_{11}O_2N$: N, 5·62
Diketone	m.p. 111–112°, lemon-yellow crystals. Found: C, 81·87; H, 4·37	Calcd. for $C_{14}H_8O_2$: C, 80·80 H, 3·84	m.p. 109°, yellow needles. Calcd. for $C_{16}H_{10}O_2$: C, 81·8 H, 4·28
Monoxime	m.p. 176°, red crystals. Found: N, 5·79, 5·89	Calcd. for $C_{14}H_9O_2$(sic)[8]: N, 6·26	Calcd. for $C_{16}H_{11}O_2N$: N, 5·63

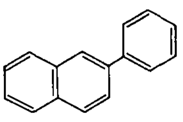
The mechanism of formation of 2-phenylnaphthalene (XI) from (IX) and (X) appears to involve a series of changes; it is evident that rearrangements must be involved (since direct substitution would yield dibenzylacetylene, $C_{16}H_{14}$), and also a dehydrogenation, since 2-phenylnaphthalene has the molecular formula $C_{16}H_{12}$. Until further studies (which we hope to describe in future communications) are complete, we defer a complete discussion of the mechanism: we think it likely, however, that the intermediary formation of 2,3-diphenylbutadiene is involved; this is known[19] to



IX

$CH_3COOCH_2C{\equiv}CCH_2OCOCH_3$

X



XI

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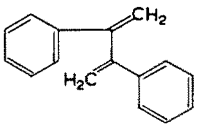
[16] F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.* **65**, 873 (1894).

[17] D. H. Hey and S. E. Lawton, *J. Chem. Soc.* 374 (1940).

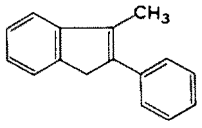
[18] Present work.

[19] W. Hausmann and A. E. Wilder Smith, *J. Chem. Soc.* 1030 (1949).

isomerize to (XIII) in presence of hydrogen chloride (produced during the synthesis

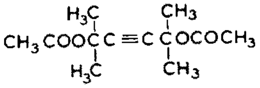


XII



XIII

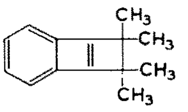
of the 102° hydrocarbon). Conversion of (XIII) to (XI) may be effected by dehydrogenation[20] and ring expansion in presence of aluminum chloride or some other similar Lewis acid. We were led by such mechanistic reasoning to the conclusion that the synthesis of a hydrocarbon from (XIV)—i.e. the tetramethyl analog of (X)—by



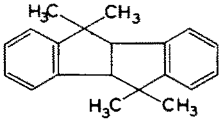
$$CH_3COO\overset{H_3C}{\underset{H_3C}{C}}C\equiv C\overset{CH_3}{\underset{CH_3}{C}}OCOCH_3$$

XIV

the procedure of Lagidze and Petrov should lead not to the structure (XV) as postulated by Lagidze and Loladze,[21] but most probably to the known hydrocarbon (XVI).[22] Very recently we have been successful in showing that this is so, and these studies will be described in Part II of this series.[23]



XV



XVI

EXPERIMENTAL

But-2-yne-1,4-diol diacetate (X)

Forty-eight grams of but-2-yne-1,4-diol* (recrystallized from ethyl acetate) was dissolved in 90 g of pyridine that had been dried over potassium hydroxide. Benzene (112 ml, reagent grade) was added as solvent, followed by 123 g of acetic anhydride in small portions, with agitation and cooling in ice (the temperature was maintained below 30°). When addition was complete, and heat evolution had ceased, the solution was poured on to cracked ice, and the mixture was shaken vigorously and allowed to separate into two phases. The organic layer was washed with 8% sodium hydroxide (2 × 125 ml), 7% hydrochloric acid (2 × 125 ml) and cold water (100 ml) and dried over anhydrous magnesium sulfate. Filtration, evaporation of the solvent by aspiration at room temperature and then fractional distillation (nitrogen in capillary) gave a clear colorless liquid, which easily crystallized at room temperature to give colorless

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* We are indebted to Messrs. General Aniline and Film Corporation for the donation of part of this material.

[20] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Amer. Chem. Soc.* **66**, 1536 (1944).

[21] R. M. Lagidze and N. R. Loladze, *Soobshchenya Akad. Nauk Gruzin. SSR* **16**, 607 (1955); *Chem. Abstr.* **50**, 11960b (1956).

[22] J. G. Smith and G. F Wright, *Canad. J. Chem.* **32**, 729 (1954).

[23] J. E. H. Hancock and D. R. Scheuchenpflug, *J. Amer. Chem. Soc.* In press.

needles of the diacetate, melting at approximately 30–32° (m.p. 28° and 31–32°).[24,25] The above run distilled at 135–135·5°/18 mm (b.p. 106°/3 mm, 122–123°/10 mm);[26,27] n_D^{20} 1·4538 (n_D^{20}1·4547 and 1·4611).[25,27] Yield, 56·0 g, 55 per cent. The poorest yield was 29 per cent and the best 68 per cent; a good yield is usually obtained if heat is evolved during the addition of the acetic anhydride (i.e. cooling should not be too great), and also if redistilled acetic anhydride is used.

Aluminum chloride

This was sublimed under dry nitrogen at 180–200° in a special apparatus, and the sublimed product was sealed off until ready for use. Recovery rarely exceeded 40–50 per cent of the original (crude) chloride, even when reagent-grade material was employed.

Procedure for alkylation[8]

Sublimed aluminum chloride (98·0 g, powdered immediately before use) and benzene (107·0 g, redistilled) were mixed with moderate stirring under nitrogen. The diacetate (61·0 g) of but-2-yne-1,4-diol was added dropwise from a separating funnel: the mixture immediately became orange-red, and slowly changed to a darker red. Evolution of heat was counteracted by cooling to maintain the temperature below 30°. When addition was complete, the separating funnel was replaced by a reflux condenser, calcium chloride tube and a trap for hydrogen chloride. The dark brown mixture was warmed in a water bath at 40–45°, with evolution of hydrogen chloride, and heating at this temperature was continued for 1 hr and then at 80–85° (thermometer in liquid) for 10 hr. The thick dark red liquid was poured into 2 N hydrochloric acid (ca. 1 l.) with cooling below 40°. This mixture was repeatedly extracted with ether, and the extracts were combined, washed with 10% sodium bicarbonate solution and with water, and then dried over anhydrous magnesium sulfate. After the solution had been filtered, volatile matter was removed by evaporation at room temperature, and the residue was distilled *in vacuo* (nitrogen in capillary) through a 6 in. Vigreux column. The fractions obtained were kept under nitrogen at 0° (see Table 2).

TABLE 2.—PRODUCTS OBTAINED FROM THE CONDENSATION OF BUT-2-YNE-1,4-DIOL DIACETATE WITH BENZENE IN PRESENCE OF ALUMINUM CHLORIDE

Fraction	Description	B.p.	Yield (g)
1	Colorless liquid	105–110°/3 mm	34·0
2	Pale green liquid	93–96°/0·15 mm	0·2
3	Pasty green mixture	105–110°/0·1 mm	0·4
4	Cream-colored solid	114–126°/0·1 mm	2·7
5	White solid	129–135°/0·1 mm	0·8
6	Undistillable Dark brown tar		ca. 25

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[24] G. Dupont, R. Dulou, et G. Lefèbvre, *Bull. Soc. Chim. Fr.* 816 (1954).

[25] I. M. Gverdtsiteli and Sh. G. Mikadze, *Zh. Obshchei Khim.* **22**, 1401 (1952); *Chem. Abstr.* **47**, 6338f (1953).

[26] W. Reppe *et al.*, *Liebigs Ann.* **596**, 57 (1955).

[27] A. W. Johnson, *J. Chem. Soc.* 1011 (1946).

Fraction 1 solidified to a mass of needles, m.p. ca. 28–31°, on being kept at room temperature, and gave a negative halogen test and hence no 4-acetoxy-1-chlorobut-2-yne was present (compare Lagidze and Petrov,[8] the paper in which this substance was reported). Fractions 4 and 5 were combined and recrystallized twice from ethanol, dissolved in hexane, and chromatographed on alumina (Merck reagent grade, for chromatography: 20 to 1 ratio of alumina to adsorbate). A third crystallization from ethanol provided a total of 0·4 g of pearly plates, melting at 102–103°; yield, 1·1 per cent over-all, or 2·5 per cent if recovered diacetate is taken into account. The crystals fluoresced blue in ultraviolet light, and gave a depression (m.p. 93–96·4°) when mixed with a sample of phenanthrene (m.p. 100°).

2-Phenylnaphthalene (XI)

The method of Elks and Hey[14] was used, with modification. To a stirred cooled mixture of 225 ml of concentrated hydrochloric acid, 250 ml of water and 72 g of 2-naphthylamine, 34·0 g of sodium nitrite was added slowly, the temperature being maintained below 5°. The solution of the diazonium salt was filtered, and then added to a solution of 80·0 g of dimethylamine and 30·0 g of anhydrous sodium carbonate in 150 ml of water. The dark brown solid obtained was filtered off, washed with water and dried in the air (110·0 g). The crude material was purified as follows: the dark brown triazene (20·0 g) was warmed gently with *n*-hexane (350 ml), and the solution was cooled to room temperature and filtered. Some insoluble tan-colored residue (1·8 g, m.p. greater than 200°) remained, and the soluble portion was chromatographed on alumina (as above, for the alkylation product). Hexane eluted 16·6 g of orange solid, m.p. 54–56°, which was crystallized from hexane (1 ml per g) at 0° with 80 per cent recovery per crystallization. After two crystallizations, and washing with ice-cold hexane, 13·2 g of once-chromatographed triazene gave 7·27 g of 1-(2-naphthyl)-3,3-dimethyltriazene as a cream-colored solid, m.p. 56–57° (m.p. 57–58°).[14] The pure triazene becomes orange and red on the surface upon exposure to air, and is best stored under nitrogen.

During the chromatographic purification, several orange-red bands remained on the column, and were only removed by stronger eluting agents. Examination of these substances is in progress.

The purified triazene (5·7 g) was dissolved in benzene (55 ml, reagent grade) and the mixture was heated to boiling. Glacial acetic acid (7·5 ml) was added, and the mixture was heated under reflux for 36 hr (shorter periods gave unchanged triazene). Removal of volatile materials and chromatography as before provided 0·97 g of a pale yellow solid, which was recrystallized from ethanol to give 2-phenylnaphthalene (0·45 g, 13 per cent) as lustrous white plates, m.p. 101·5–102·5° (m.p. 102°).[14] The usual orange-red bands were also recovered from the chromatogram.

Samples of pure alkylation product (m.p. 102–103°) and of the 2-phenylnaphthalene were mixed intimately: this mixture showed no depression of m.p.

Spectral data

The ultraviolet absorption spectra were obtained with a Cary model 11-MS ultraviolet spectrometer: 2-phenylnaphthalene prepared by the alkylation reaction showed λ_{max} 248 and 286 mμ in methyl*cyclo*hexane; ε_{max} 54,000 and 11,000 (λ_{max} 250 and 285 mμ in *cyclo*hexane; ε_{max} 50,000 and 11,000 respectively).[15] Maxima were also detected at 355 and at 373 mμ; these correspond to the presence of anthracene in concentrations of approximately 0·1–0·5 per cent of the whole. This latter explanation is supported by the fact that in the mass spectrum of the alkylation product there were peaks in the region m/e 178, although not of large magnitude. In view of the small amounts at our disposal, no attempt was made to pursue this matter.

The infrared absorption spectra were obtained by using a double-beam infrared spectrometer with a rock-salt optical system, designed and built by L. W. Herscher. The spectra were run in 2 per cent solution in carbon tetrachloride from 2·5–7·5 μ and in 2 per cent solution in carbon disulfide from 7·5–16 μ. Bands were noted at 3·27 (ms), 3·30(m), 6·24(s), 6·66(s), 6·80(m), 6·85(m), 6·97(w), 7·40(w), 7·89(w), 8·83(m), 9·28(m), 9·77(m), 10·40(m), 10·55(m), 11·22(s), 12·23(s), 12·98(s), 13·19(s), 13·52(ms) and 14·37(s) μ(s = strong, m = medium, w = weak).

Mass spectra were obtained using a 90° sector mass spectrometer: a parent peak at m/e 204 was noted, plus lower molecular-weight fragments characteristic of a phenylnaphthalene.

Acknowledgements—This research has been facilitated by the kind help of Mrs. V. Krivoshein, Dr. Frank Munk (Reed College) and Mrs. V. Tolkmith (Main Library, The Dow Chemical Company, Midland, Michigan), who rendered willing service in translation. We received invaluable assistance from Dr. J. D. Head (Executive Research) and Mr. W. J. Potts (Spectroscopy Laboratories) of the Dow Chemical Company in obtaining the infrared, ultraviolet and mass-spectrometric data. We wish to express our sincere appreciation to Prof. R. M. Lagidze, Tbilisi State University, Georgia, U.S.S.R., for sending us considerable information, and finally to the Research Corporation of New York for a Frederick Gardner Cottrell grant which defrayed the expenses of this investigation.