1°, and then was poured into iced water acidified with hydrochloric acid. The organic layer was separated and after drying over calcium chloride the unchanged ethylene chloride, which weighed 755 g., was removed by distillation. The residue was now fractionally distilled under vacuum of 10 mm. and several fractions were obtained.

The fractions I and III crystallized after a day.

The crystals obtained from fraction I were recrystallized three times from alcohol until the melting point was fixed at 51.7–52.0°. This compound was proved to be identical with bibenzyl by a mixed melting point with a known sample.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.87.

The repeated recrystallizations of the crystals from the fraction III afforded a sample of a melting point of 56.7–57.4°. This agrees in properties with *m*-bis-(β-phenylethyl)-benzene and, when admixed with an authentic specimen, did not depress the melting point, thus proving the identity.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.49.

Summary

By the action of anhydrous aluminum chloride ethylene chloride yields bibenzyl, *m*-bis-(β-phenylethyl)-benzene and finally a polycondensation product.

This phenomenon is explained that at first benzene is formed from ethylene chloride. The resultant benzene then condenses with the excess of ethylene chloride in the sense of the Friedel–Crafts reaction.

KYOTÔ, JAPAN RECEIVED NOVEMBER 23, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYÔTO UNIVERSITY]

The Organic Reactions with Aluminum Chloride. XXI. The Cycli-alkylation of Benzene with 1,4-Dibromo-2-butene and the Disproportionation of Hydrogen Atoms

BY KEIITI SISIDO AND HITOSI NOZAKI

The Friedel–Crafts reactions of poly-functional alkylating agents with benzene are often associated with various anomalies, for example, the "cycli-alkylation"[1] and the shift or reduction of halogen atoms.[2] The former reaction may be of unusual interest as a simple method of synthesizing the compounds of polynuclear structures. In continuation of the studies in this field, we have investigated the condensation of 1,4-dibromo-2-butene with benzene.

The dibromobutene dissolved in a large excess of benzene was treated with aluminum chloride at ordinary temperature. Upon fractional distillation of the reaction products, tetralin and 2-phenyl-1,2,3,4-tetrahydronaphthalene were found to have been formed along with a considerable amount of tarry matter. Neither naphthalene nor dihydronaphthalene was produced. Phenyl-substituted butanes which might be expected as a result of the ordinary Friedel–Crafts reaction also failed to be detected.

These observations may indicate that the first stage of the reaction consists in the condensation of one mole of benzene with one mole of the dibromobutene forming 1,4-dihydronaphthalene under the cyclization by the 2-butene residue. As 1,4-dihydronaphthalene rearranges, however, easily into 1,2-dihydro-compound, for example, by the action of sodium ethylate,[3] the hydrogen atoms at the 1,4-position are supposed to be labile. It seemed to us, therefore, necessary to examine the action of aluminum chloride upon 1,4-dihydronaphthalene in order to clarify the mechanism of this condensation.

To a solution of the dihydronaphthalene in benzene was added aluminum chloride and the mixture was allowed to react at ordinary temperature. It was noted that only small quantities of 2-phenyl-1,2,3,4-tetrahydronaphthalene were produced. The main product was found to be a mixture of about equal amounts of naphthalene and tetralin. We have repeated the same experiment introducing hydrogen chloride gas into the reaction mixture and achieved the same result. Treating 1,4-dihydronaphthalene alone with aluminum chloride we obtained also naphthalene and its tetrahydride.

We have also investigated the reaction of aluminum chloride with 1,2-dihydronaphthalene. In addition to considerable amounts of higher-boiling substances there resulted also in this case naphthalene and tetralin in almost equal quantities. Scott and Walker,[4] who studied the nature of the polymerized dihydronaphthalene as a synthetic resin, stated that 1,2-dihydronaphthalene gave, upon treatment with aluminum chloride, a red brittle resin having a molecular weight of 388 as well as a viscous oil, apparently a dihydronaphthalene dimer. We have found that the 1,2-isomer gives more resinous matter than the 1,4-compound.

Among the reaction products of the 1,4-dihydronaphthalene was a higher-boiling fraction, whose elementary analysis indicated the formula $C_{20}H_{20}$, from which, after a week, crystals of composition $C_{20}H_{18}$ separated. As the original fraction upon sulfur-dehydrogenation, gave 2,2′-binaphthyl in a good yield, it is supposed that the fraction consists of a mixture of 1,2,3,4-tetrahydro-2,2′-binaphthyl, $C_{20}H_{18}$, and 1,2,3,4,1′,2′,3′,4′ - (or 1,2,3,4,5′,6′,7′,8′) - octahydro - 2,2′ - bi-

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[1] Bruson and Kroeger, THIS JOURNAL, **62**, 36 (1940); see also Price, Chapin, Goldman, Krebs and Shafer, *ibid.*, **63**, 1857 (1941).

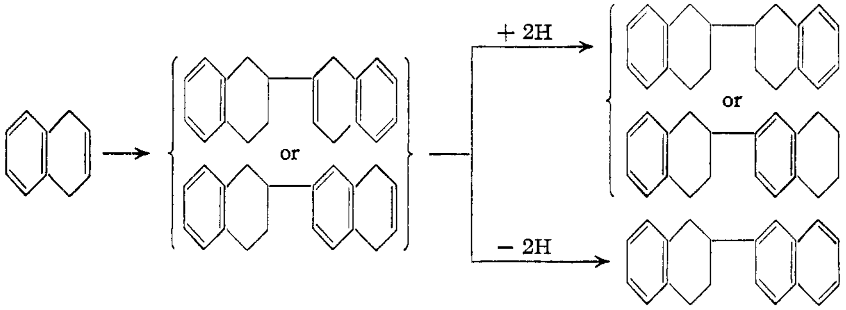
[2] Sisido and Nozaki, *ibid.*, **69**, 961 (1947).

[3] Straus and Lemmel, *Ber.*, **54**, 25 (1921).

[4] Scott and Walker, *Ind. Eng. Chem.*, **32**, 312 (1940).

naphthyl,[5] $C_{20}H_{22}$. This mixture may arise, in our opinion, from the dimer of 1,4-dihydronaphthalene by the disproportionation of hydrogen atoms as shown in the figure. As we could, however, neither isolate the octahydrobinaphthyl nor establish the constitution of the tetrahydro compound, this mechanism has not been proved.

Although we have not characterized the polymers of 1,2-dihydronaphthalene, bisdialin, *i.e.*, tetralino-1,2;2′,1′-(or 1,2;1′,2′)-tetralin of v. Braun and Kirschbaum[5] obtained by the sulfuric acid treatment of this dihydronaphthalene, is to be noticed.



In the Friedel–Crafts reaction of allyl chloride with benzene Nenitzescu and Isacescu[6] obtained 1-phenylpropane as well as 1,2-diphenylpropane and they supposed the formation of 2-chloro-1-phenylpropane as an intermediate. The present condensation of 1,4-dibromo-2-butene with benzene bears a close resemblance to this reaction: in both cases the reduction takes place only at the olefinic double bond and such a reaction product, as, for example, chloroisopropylbenzene or dibromobutylbenzene, respectively, in which only an addition of benzene at the double bond occurred, is not obtained.

As to these facts Nenitzescu and others explained that in the case of the transference of hydrogen by the effect of aluminum chloride the double bond does not act immediately as the acceptor. At first hydrogen chloride adds to the double bond and the chlorine atom is replaced by phenyl radical or by hydrogen atom. This statement holds also for the elucidation of the mechanism of the condensation of 1,4-dibromo-2-butene with benzene. But, since the reaction of dihydronaphthalenes and aluminum chloride consists, at least partly, in the disproportionation of labile hydrogens and since hydrogen chloride plays apparently no role in this case, the possibility that the double bond does act as a hydrogen acceptor, contrary to the opinion of Nenitzescu and others,[6] should be considered.

Experimental[7]

The Friedel–Crafts Reaction of 1,4-Dibromo-2-butene with Benzene.—To a suspension of 12 g. of freshly powdered aluminum chloride in 90 g. of benzene at 24–27° was added with stirring during about four hours a solution of 38 g. of 1,4-dibromo-2-butene prepared from butadiene and bromine, in 50 g. of benzene. The resulting mixture was stirred for an additional three hours at the same temperature. On working up the product in the usual way, there were obtained several fractions:

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I_1	95–115	34	4.3	Colorless oil
II_1	145–175	6	4.9	Yellowish oil
III_1	190–230	6	5.3	Yellow, viscous sirup
IV_1	Residue	..	8.7	Reddish brown resin

Tetralin.—Upon redistillation under ordinary pressure Fraction I_1 came over at 200–210°.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.50.

This fraction gave no picrate and did not add bromine at −20°; hence, it was concluded that it contained neither naphthalene nor dihydronaphthalene.

When a mixture of 1.3 g. of fraction I_1 and 0.7 g. of sulfur was heated to 200–230° for three and a half hours, there was obtained 0.9 g. of naphthalene, m. p. and mixed m. p. 80°; picrate, m. p. and mixed m. p. 151°.

A solution of 0.4 g. of fraction I_1 in 10 cc. of carbon disulfide was added to 0.8 g. of aluminum chloride and 0.4 g. of phthalic anhydride. The mixture was refluxed for three hours on a water-bath. There resulted 0.5 g. of *o*-(1,2,3,4-tetrahydro-6-naphthoyl)-benzoic acid, m. p. and mixed m. p. 153–155°.[8]

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.03; H, 6.06.

2-Phenyl-1,2,3,4-tetrahydronaphthalene.[9]—Fraction II_1 gave analytical figures which agreed with $C_{16}H_{16}$; d^{20}_4 1.0436.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.58; H, 7.70.

When 1.2 g. of Fraction II_1 was heated to 220° with 0.4 g. of sulfur for four hours and the resulting melt was distilled under reduced pressure, there was obtained 0.7 g. of substance, m. p. 101°. A mixture of this product and 2-phenylnaphthalene of m. p. 101°, prepared from β-naphthylamine according to Hey and Lawton[10] melted without depression.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.75; H, 6.05.

In further identification of the dehydrogenation product it was oxidized with chromic anhydride and acetic acid to 2-phenyl-1,4-naphthoquinone,[11] which was obtained as yellow needles, m. p. 109–110°.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 81.84; H, 4.61.

To a boiling mixture of 4.0 g. of fraction II_1, 125 cc. of water and 25 cc. of concentrated sulfuric acid was added under stirring a solution of 12.2 g. of potassium permanganate in 400 cc. of water. After twenty-two hours of stirring the product was extracted with ether. The ethereal solution was washed with dilute sodium hydroxide solution, the aqueous layer separated and acidified with hydrochloric acid. The precipitates were dissolved in ether and this ethereal solution was dried and distilled to

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(5) v. Braun and Kirschbaum, *Ber.*, **54**, 597 (1921).

(6) Nenitzescu and Isacescu, *ibid.*, **66**, 1100 (1933). *Cf.* also Nenitzescu, *Z. angew. Chem.*, **52**, 231 (1939).

(7) Microanalyses by Misses Meizyô and Ogawa of our Laboratory.

(8) Underwood and Walsh, THIS JOURNAL, **57**, 940 (1935).

(9) v. Braun and Manz, *Ann.*, **468**, 258 (1926).

(10) Hey and Lawton, *J. Chem. Soc.*, 374 (1940).

(11) Chattaway and Lewis, *ibid.*, **65**, 873 (1894); Zincke and Breuer, *Ann.*, **226**, 23 (1884); Zincke, *ibid.*, **240**, 137 (1887).

remove the solvent. The residue was treated with chloroform. The insoluble portion was separated, sublimed and recrystallized from carbon tetrachloride. There were obtained colorless needles, m. p. 127–129°. A mixture of this product and phthalic anhydride melted at 129–131°. Recrystallizations of the chloroform-soluble portion after removing the solvent gave benzoic acid, m. p. and mixed m. p. 122°.

These results indicated that fraction II_1 was 2-phenyl-1,2,3,4-tetrahydronaphthalene.

Fractions III_1 and IV_1 were not investigated.

The Reaction of 1,4-Dihydronaphthalene with Aluminum Chloride.—1,4-Dihydronaphthalene was prepared by the method of Cook and Hill[12] and purified through its addition product with mercuric acetate.[13]

To 14.2 g. of 1,4-dihydronaphthalene was added at 25° under stirring 1.1 g. of aluminum chloride in small portions. The reaction temperature rose spontaneously to about 90°. After two and a half hours of stirring at 30–40° the mixture was poured onto crushed ice acidified with sulfuric acid. The product was subjected to fractional distillation.

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I_2	202–208	760	4.6	Deposited
II_2	70–110	8	1.0	crystals
III_2	205–220	7	1.1	Yellow
IV_2	300–320	6	0.6	sirup
V_2	Residue	...	...	Black mass

Separation of Naphthalene and Tetralin.—Fractions I_2 and II_2 were combined and the mixture was cooled in ice-salt mixture. The crystals separated were collected. These were found to be naphthalene, m. p. and mixed m. p. 80°; yield 2.0 g.

Anal. Calcd. for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.97; H, 6.54.

To the mother liquor was added a hot alcoholic solution of picric acid. After removing naphthalene picrate thus separated as yellow needles, m. p. and mixed m. p. 151°, the filtrate was concentrated and dissolved in ether. The ethereal solution was washed with aqueous ammonia and water. When a mixture of this solution, 5 g. of mercuric acetate and 50 cc. of water was stirred for four hours, there could not be obtained the addition product of 1,4-dihydronaphthalene with mercuric acetate. The ethereal layer was separated and washed with water. After removing ether the residue was distilled. At 200–210° tetralin came over, yield 2.1 g.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.01; H, 9.48.

A Friedel–Crafts condensation product of this oily substance with phthalic anhydride melted at 156–157°. A mixture of this product with an authentic specimen of *o*-(1,2,3,4-tetrahydro-6-naphthoyl)-benzoic acid melted without depression.

These observations show that Fractions I_2 and II_2 are a mixture of naphthalene and tetralin which does not contain 1,4-dihydronaphthalene.

The Reaction of 1,4-Dihydronaphthalene and Benzene in the Presence of Aluminum Chloride.—To a suspension of 15 g. of aluminum chloride in 100 g. of benzene at 10° was added with stirring during about two and a half hours a solution of 28 g. of 1,4-dihydronaphthalene in 73 g. of benzene. No remarkable rise of temperature was noticed. After an additional thirty minutes the stirring was stopped. The reaction product separated into two layers. The upper layer was decanted, washed and dried. After distilling off of benzene the residue was subjected to fractional distillation.

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I_3	195–217	760	8.0	Deposited
II_3	–145	7	1.1	crystals
III_3	145–170	6	1.6	Colorless oil
IV_3	200–230	6	2.0	Yellow
V_3	Residue	...	0.5	sirup

Hydrolysis of the lower layer of the reaction product gave chiefly tarry matter from which nothing could be identified.

Similar results were obtained when the reaction was carried out in a stream of hydrogen chloride gas.

Naphthalene and Tetralin.—From Fractions I_3 and II_3 were isolated and identified 3.3 g. of naphthalene as well as 3.0 g. of tetralin in the same way as described above.

2-Phenyl-1,2,3,4-tetrahydronaphthalene.—Fraction III_3 gave analytical figures which agreed with $C_{16}H_{16}$.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.71; H, 8.07.

Dehydrogenation of this fraction with sulfur yielded 2-phenylnaphthalene and these observations may indicate that Fraction III_3 is 2-phenyl-1,2,3,4-tetrahydronaphthalene.

The Reaction of 1,2-Dihydronaphthalene with Aluminum Chloride.—1,2-Dihydronaphthalene was prepared by the method of v. Braun and Kirschbaum.[5] The product melted at −8° and proved to be quite free from naphthalene.

To 13.1 g. of 1,2-dihydronaphthalene cooled at −5° was added 1.0 g. of aluminum chloride and the reaction temperature was allowed to rise; after an hour it reached 15° and after additional thirty minutes 30°. When the reaction product was treated as usual, the following fractions were obtained.

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I_4	65–80	7	2.0	Deposited crystals
II_4	200–240	7	1.5	Yellow viscous oil
III_4	Residue	..	*ca.* 6	Yellow resin

Fraction I_4 was separated into 0.5 g. of naphthalene and 0.6 g. of tetralin. Naphthalene was identified by a mixed melting point with a known sample. Tetralin was analyzed.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.47; H, 9.32.

When this product was condensed with phthalic anhydride, there was obtained *o*-(1,2,3,4-tetrahydro-6-naphthoyl)-benzoic acid, m. p. and mixed m. p. 153–155°.

The fractions II_4 and III_4 were not investigated.

Hydrogenated Derivatives of Binaphthyl.—Fractions III_2 and IV_3, that is, the fractions boiling about 200° under 6 mm. pressure of the above-mentioned aluminum chloride treatment of 1,4-dihydronaphthalene, were found to consist of the same components. Their analysis gave a figure near $C_{20}H_{20}$.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.79; H, 7.43.

When 1.2 g. of the fraction was heated at 190–240° with 0.6 g. of sulfur for five and one-half hours and the resulting mass was distilled under reduced pressure, there was obtained 1.0 g. of substance, which soon solidified. After triturating with ether to remove a small quantity of oily matter, it was recrystallized from benzene; m. p. 182°. The mixed m. p. with 2,2′-binaphthyl, prepared previously in our Laboratory, showed no depression.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.57; H, 5.98.

The picrate, orange needles, m. p. and mixed m. p. 183–184°.

The fraction became a crystalline mass after about a week of standing, which was freed from oily substance and after five recrystallizations from a mixture of alcohol and benzene gave colorless plates of m. p. 85–88°.

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[12] Cook and Hill, THIS JOURNAL, **62**, 1995 (1940).

[13] Sand and Genssler, *Ber.*, **36**, 3705 (1903).

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.30; H, 6.91.

From these results we concluded that the fraction consisted perhaps of a mixture of 1,2,3,4,1′,2′,3′,4′- (or 1,2,3,4,5′,6′,7′,8′)-octahydro-2,2′-binaphthyl and 1,2,3,4-tetrahydro-2,2′-binaphthyl in nearly equal quantities.

Summary

1. The Friedel–Crafts reaction of 1,4-dibromo-2-butene with benzene yielded tetralin as well as 2-phenyl-1,2,3,4-tetrahydronaphthalene.

2. 1,4-Dihydronaphthalene was found to change into naphthalene and tetralin in the presence of aluminum chloride.

3. An analogous reaction was observed also in the case of 1,2-dihydronaphthalene.

KYÔTO, JAPAN RECEIVED APRIL 29, 1947

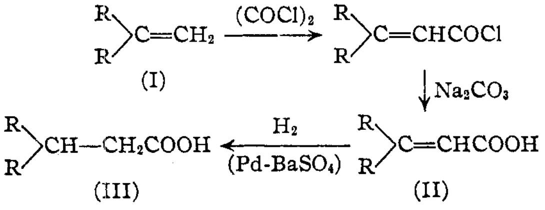
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE AND THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY, JERUSALEM]

β,β-Diarylacrylic Acids.[1] I. Synthesis and Properties of Symmetrical and Unsymmetrical β,β-Diarylacrylic Acids.

BY FELIX BERGMANN, MOSHE WEIZMANN, ELCHANAN DIMANT,[1] JOSEF PATAI[1] AND JACOB SZMUSKOWICZ

The reaction of 1,1-diphenylethylene with oxalyl chloride to form β,β-diphenylacrylyl chloride was discovered by Kharasch and co-workers.[2] As part of a program on the investigation of diarylethylenes, we have applied this reaction to a series of symmetrically and unsymmetrically substituted diphenylethylenes (I).

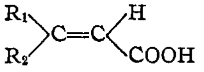
The reaction was found to be a general one; by the use of excess oxalyl chloride (3 to 5 moles) and subsequent hydrolysis of the acid chloride produced, nearly quantitative yields of β,β-diarylacrylic acids (II) were obtained. The application of the reaction to a group of symmetrical and unsymmetrical 1,1-diarylethylenes is summarized in Tables I and II. The corresponding β,β-diarylpropionic acids (III) were easily accessible by catalytic hydrogenation of the acrylic acids (Table III).



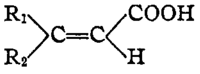
The speed of reaction was markedly influenced by the substituents present in the phenyl groups. 1,1-Di-(*p*-anisyl)-ethylene (I,3) reacted completely at room temperature within a half hour, 1,1-diphenylethylene (I,1) had to be refluxed with oxalyl chloride for about two hours, and 1,1-di-(*p*-bromophenyl)-ethylene (I,6) required about eighteen hours for completion of the reaction. The susceptibility of dianisylethylene to substitution by the —COCl group was so great that phosgene in boiling benzene converted it to the dianisylacrylic acid.

The electronic influence of the substituents also influenced the uncatalyzed decarboxylation of the diarylacrylic acids: while the β,β-diphenylacrylic acid (II,1) was stable at 200° and suffered only very slow decarboxylation at 250°, the β,β-di-(*p*-anisyl)-acrylic acid (II,3) was slowly decarboxylated by boiling a solution of it in acetic acid or even by boiling its aqueous suspension. The β-phenyl-β-*p*-anisylacrylic acid was intermediate in stability; carbon dioxide was eliminated from it at about 200°. These results give an explanation of the observation of Bergmann and Bondi[3] that dianisylethylene does not yield a phosphinic acid with phosphorus pentachloride.

When unsymmetrical 1,1-diarylethylenes were refluxed with oxalyl chloride and the mixture hydrolyzed, the two possible isomers (IIα and IIβ) were obtained in most cases.



(IIα)



(IIβ)

The use of a large excess of the chloride produced this mixture in good yields, but unavoidable losses during the laborious separation procedures permitted only an approximate estimate of the relative proportion of the two isomers (Table II).

1-Phenyl-1-(*p*-fluorophenyl)-ethylene (I,8) gave rise to a single form of β-phenyl-β-(*p*-fluorophenyl)-acrylic acid (II,8) in nearly quantitative yield; 1-(*p*-tolyl)-1-(*p*-fluorophenyl)-ethylene (I, 11) likewise yielded only one form of the corresponding acid (II,11). On the other hand, the *p*-chloro and *p*-bromo derivatives (II,9 and II,10) were obtained as nearly equimolar, sharply melting mixtures of the two isomers. Resolution of each mixture into the individual isomers showed that the individual melting points lay close to each other and were both higher than that of the mixture.

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[1] Part of theses submitted to the Hebrew University, Jerusalem 1947, by Elchanan Dimant and Josef Patai.

[2] Kharasch, Kane and Brown, THIS JOURNAL, **64**, 333 (1942).

[3] E. Bergmann and Bondi, *Ber.*, **63**, 1158 (1930); *ibid.*, **64**, 1455 (1931); *cf.* also Kosolapoff and Huber, THIS JOURNAL, **68**, 2540 (1946).