

## Stable Organic Free Radicals. I. Synthesis of Substituted $\alpha,\gamma$ -Bisdiphenylene- $\beta$ -phenylallyls

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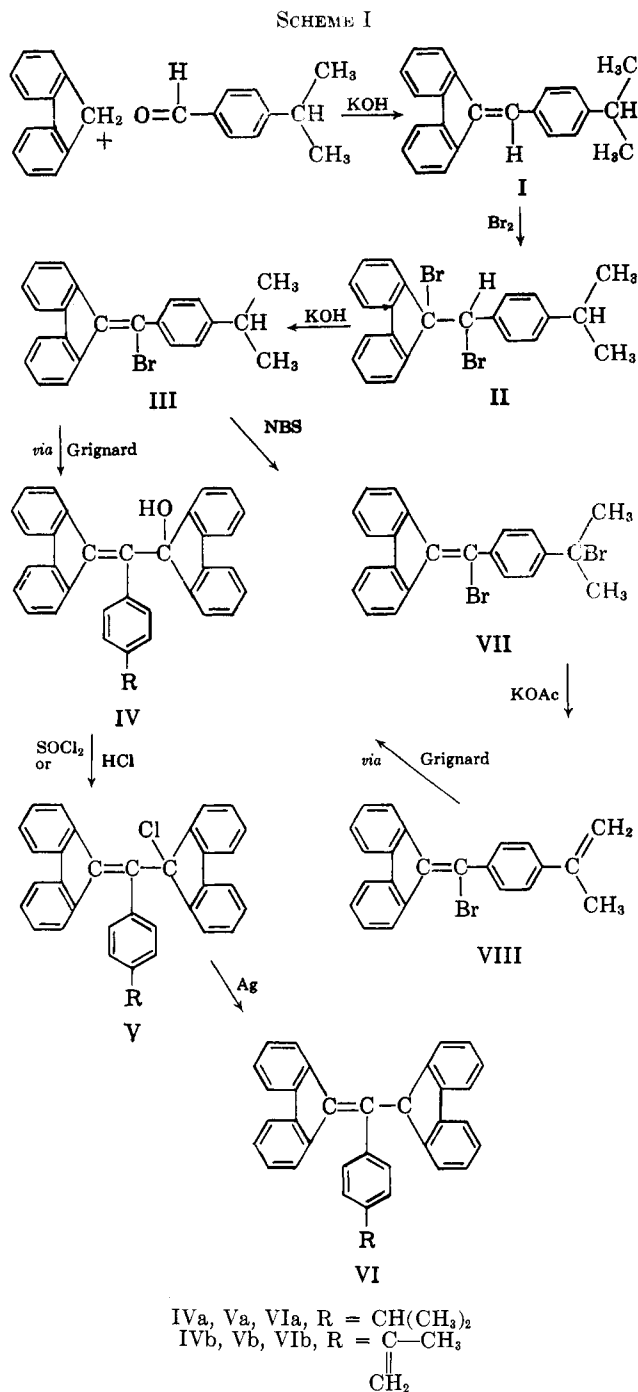
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In connection with our study of paramagnetism of organic free radicals, two new stable free radicals,  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl,  $C_{36}H_{27}$  (BDIPA), and its isopropenyl analog,  $C_{36}H_{25}$  (BDIPAM), were prepared by the general procedure, with some modification, followed by Koelsch<sup>1</sup> in the synthesis of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -phenylallyl (BDPA).

The synthesis of BDIPA, outlined in Scheme I, was fairly straightforward. No difficulty was experienced in the alkaline condensation of *p*-isopropylbenzaldehyde with fluorene to give *p*-isopropylbenzalfluorene (I) followed by addition of bromine to form the dibromide II. Dehydrohalogenation with potassium hydroxide led to  $\alpha$ -(*p*-isopropylphenyl)- $\beta$ -diphenylenevinyl bromide (III). This compound readily formed the Grignard reagent, which upon addition of 9-fluorenone, yielded  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl alcohol (IVa) which is converted to the chloride V<sub>a</sub> by reaction with dry hydrogen chloride. Dehalogenation of V<sub>a</sub> in the usual manner, by mercury in benzene, or benzene-ether, yielded a product containing mercury which could not be removed by recrystallization. When the reaction was carried out with powdered silver in tetrahydrofuran, an easily crystallizable pure free radical VI<sub>a</sub> was obtained.

In the preparation of this isopropenyl analog VI<sub>b</sub> the vinyl bromide III is further brominated with *N*-bromosuccinimide to  $\alpha$ -[*p*-(2-bromoisopropyl)phenyl]- $\beta$ -diphenylenevinyl bromide (VII). This can be dehydrohalogenated with potassium acetate in glacial acetic acid to  $\alpha$ -(*p*-isopropenylphenyl)- $\beta$ -diphenylenevinyl bromide (VIII) in good yield. It is possible to prepare the latter product by brominating II with *N*-bromosuccinimide and carrying out both dehydrohalogenations simultaneously using alcoholic potassium hydroxide. However, the yield in this case is very poor due to the difficulty in purifying both the intermediate tribromide and the final product VIII which is contaminated with tarry by-products.

The Grignard reaction with VIII was extremely slow and gave low yields. Several attempts were made to speed up the reaction and improve the yield by modification of the conventional Grignard procedure. The use of lithium generally resulted in reduction of 9-fluorenone to the pinacol. Since the solubility of III in diethyl ether is quite low, several other solvent systems were tried, but either there was no reaction at all or unidentifiable tars were recovered. The best results were obtained with high speed stirring (10,000–15,000 r.p.m.) and slow addition of the vinyl bromide to the activated magnesium. Even under these conditions, the reaction with magnesium required eighteen to twenty-two hours. Addition of 9-fluorenone, followed by decomposition with ammonium chloride, gave the tertiary alcohol IV<sub>b</sub>. Replacement of the hydroxyl



was accomplished by treatment with thionyl chloride in the presence of pyridine. The resulting chloride V<sub>b</sub> was dechlorinated with powdered silver to give the free radical VI<sub>b</sub>.

The infrared spectra of the free radicals confirm the presence of the isopropenyl group in BDIPAM as shown by the absorption band at 895  $cm^{-1}$  which is due to  $CR_1R_2=CH_2$ . The BDIPA spectrum has no band in this region. Like  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -phenylallyl the two new stable free radicals have a bright green metallic luster by reflection and an orange brown color by transmission. They are very stable in solid form and decompose slowly in solution when exposed to air. A comparison of some of the magnetic characteristics of these radicals with those of BDPA is shown in Table I.

(1) C. F. Koelsch, *J. Am. Chem. Soc.*, **54**, 4744 (1932).

TABLE I

	Line width <sup>a</sup> (gauss)	$\rho$ -Value <sup>b</sup>	$\tau_{1/2}$ <sup>c</sup> (min.)
BDPA	0.64	2.0026	10.55
BDIPA	3.10	2.0026	49.02
BDIPAM	0.66	2.0026	18.49

<sup>a</sup> Width at maximum slope (at 27.5°). <sup>b</sup> Free electron value = 2.0023. <sup>c</sup> Time for signal strength to decrease to one-half its maximum value in a 0.005 *M* solution in benzene when exposed to air.

The electron paramagnetic hyperfine structure of these radicals appears to be identical with that of BDPA, thus supporting the hypothesis of Hausser<sup>2</sup> that the free electron is interacting with eight equivalent protons in the fluorenyl rings but not with the protons in the  $\beta$ -phenyl ring.

A more complete discussion of the magnetic characteristics of BDIPA and BDIPAM will be presented in another paper.

### Experimental<sup>3</sup>

***p*-Isopropylbenzalfluorene (I).**—A mixture of 84 g. (0.57 mole) of *p*-isopropylbenzaldehyde, 100 g. (0.60 mole) of fluorene, and 12 g. of crushed potassium hydroxide in 200 ml. of *p*-xylene was refluxed with stirring for 4 hr. The evolved water (approximately 10 ml.) was collected in a trap. The mixture was then cooled to room temperature and poured over 100 g. of crushed ice. The organic layer was separated, washed with water until neutral, and dried over anhydrous sodium sulfate. The solution was then evaporated under vacuum to remove the solvent. The viscous residue was washed with alcohol and dried. The yield of crude product was 116.5 g. (72%).

This product could be distilled at 252 to 256° (1.5 to 2.0 mm.), to give a viscous, yellow oil.

*Anal.* Calcd. for C<sub>23</sub>H<sub>20</sub>: C, 93.20; H, 6.80. Found: C, 93.14; H, 6.75.

***p*-Isopropylbenzalfluorene Dibromide (II).**—To a solution of 99.2 g. (0.34 mole) of *p*-isopropylbenzalfluorene in 100 ml. of acetic acid, 55 g. of bromine in 55 ml. of acetic acid was added by drops while keeping the temperature of the reaction mixture at 25 to 30°. When the addition was completed, the mixture was cooled to 15° and filtered. The solid product was washed with 50 ml. of cold acetic acid, 50 ml. of 75% aqueous acetic acid, 50 ml. of 50% aqueous acetic acid, and finally with water. After vacuum drying, the yield of crude dibromide was 135.1 g. (84.7%). Recrystallization from acetic acid gave pale yellow plates, m.p. 142.5–143.5°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>18</sub>Br<sub>2</sub>: C, 60.55; H, 4.42; Br, 35.03. Found: C, 60.36; H, 4.55; Br, 35.10.

**$\alpha$ -(*p*-Isopropylphenyl)- $\beta$ -diphenylenevinylbromide (III).**—A solution of 68.4 g. (0.15 mole) of *p*-isopropylbenzalfluorene dibromide in 150 ml. of ethanol was heated to reflux. To this was added a solution of 15.0 g. (0.23 mole) of 87% potassium hydroxide in 50 ml. of ethanol and 7.5 ml. of water. The mixture was refluxed for 30 min., cooled, and poured over 100 g. of cracked ice. The solid precipitate was filtered off, washed with water, and dried in the vacuum oven. The product was recrystallized from heptane. The yield was 45 g. (75%), m.p. 105–106.5°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>Br: C, 73.60; H, 5.10; Br, 21.30. Found: C, 73.69; H, 4.65; Br, 21.38.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl Alcohol (IVa).**—Magnesium turnings (4.68 g., 0.20 g.-atom) and a few crystals of iodine were heated in a nitrogen atmosphere until the iodine was vaporized. After cooling, the system was flushed with dry nitrogen and a solution of 75 g. (0.20 mole) of  $\alpha$ -*p*-isopropylphenyl)- $\beta$ -diphenylenevinyl bromide in 1200 ml. of dry ether was added. The mixture was refluxed with rapid stirring for 6.5 hr., at which time the magnesium was essentially consumed. To this mixture was added a solution of 36 g. (0.20 mole) of 9-fluorenone in 300 ml. of dry ether. After 30 min. of reflux, with stirring,

the yellow suspension was cooled and filtered, and the solid product was decomposed with ice-cold saturated ammonium chloride solution. The mixture was warmed to remove excess ether and filtered. The solid product was washed with water and ethanol and then vacuum dried. Recrystallization from benzene gave 40 g. (42.1%) of light yellow crystals, m.p. 152.5–153.5°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>28</sub>O: C, 90.72; H, 5.93. Found: C, 90.72; H, 5.95.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(*p*-isopropenylphenyl)allyl Alcohol (IVb).**—Magnesium turnings (2.75 g., 0.11 g.-atom) were activated as in IVa. After flushing the system with dry nitrogen, 1800 ml. of dry ether was added. The ether was refluxed through a Soxhlet extractor containing 42.5 g. (0.11 mole) of  $\alpha$ -(*p*-isopropenylphenyl)- $\beta$ -diphenylenevinyl bromide in order to add the slightly soluble halide slowly. Rapid stirring was essential to get reasonable yields. The rate of reflux was adjusted to complete the addition in 8–10 hr. The reaction was completed in 18–22 hr. To the Grignard solution was then added 20 g. (0.11 mole) of 9-fluorenone in 200 ml. of dry ether. After 45 min. the light orange suspension was cooled to room temperature and filtered. The residue was worked up as in IVa and then recrystallized from heptane to give 24.7 g. (48%) of light yellow crystals, m.p. 162–163°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>28</sub>O: C, 91.11; H, 5.52. Found: C, 90.86; H, 5.51.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl Chloride (Va).**—A solution of 3 g. (0.0063 mole) of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl alcohol in 75 ml. of dry benzene was cooled to 5°. Powdered, anhydrous calcium chloride (0.5 g.) was added, and then a slow stream of hydrogen chloride gas was bubbled through the stirred mixture for 1 hr. The excess hydrogen chloride was removed by evacuating with an aspirator for 10 min. The solution was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated at room temperature to 10 ml. The residual solution was diluted with 50 ml. of hexane and the pale tan precipitate was filtered off and washed with hexane. Recrystallization from 1:1 hexane-benzene gave 1.3 g. (41%, m.p. 166–168°).

*Anal.* Calcd. for C<sub>28</sub>H<sub>27</sub>Cl: C, 87.34; H, 5.50; Cl, 7.16. Found: C, 87.16; H, 5.42; Cl, 6.92.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(*p*-isopropenylphenyl)allyl Chloride (Vb).**—A suspension of 7 g. (0.015 mole) of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -(*p*-isopropenylphenyl)allyl alcohol in 300 ml. of carbon tetrachloride containing 2.5 g. (0.031 mole) of pyridine was cooled to 5°. To this was slowly added 2.1 g. (0.018 mole) of thionyl chloride in 20 ml. of carbon tetrachloride. The mixture was stirred for 2 hr. at 5–10° and then evaporated to dryness under vacuum. The residue was washed with water and methanol and dried. Recrystallization from 1:1 hexane-benzene gave 4 g. (54%) of tan crystals, m.p. 182–184° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>25</sub>Cl: C, 87.70; H, 5.11; Cl, 7.19. Found: C, 87.71; H, 5.13; Cl, 7.09.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl (VIa).**—This preparation was carried out in a drybox under a nitrogen atmosphere. A solution of 4 g. (0.008 mole) of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -(*p*-isopropylphenyl)allyl chloride in 150 ml. dry tetrahydrofuran was shaken with 9 g. (0.083 mole) of silver powder for 5 hr. at room temperature. The reaction mixture was filtered and the residue was washed with tetrahydrofuran. The combined filtrates were evaporated to dryness and the product was recrystallized from methylcyclohexane to give 2 g. (52%) of bright green metallic needles, m.p. 189–190°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>27</sub>: C, 94.08; H, 5.92. Found: C, 93.90; H, 5.65.

**$\alpha,\gamma$ -Bisdiphenylene- $\beta$ -(isopropenylphenyl)allyl (VIb).**—The preparation for this compound was carried out in the same way as for VIa. The yield was 2.5 g. (65%) of dark green metallic needles, m.p. 197–199°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>25</sub>: C, 94.49; H, 5.51. Found: C, 94.47; H, 5.65.

**$\alpha$ -(*p*-2-Bromoisopropylphenyl)- $\beta$ -diphenylenevinyl Bromide (VII).**—A mixture of 31 g. (0.08 mole) of  $\alpha$ -(*p*-isopropylphenyl)- $\beta$ -diphenylenevinyl bromide, 14.8 g. (0.08 mole) of *N*-bromosuccinimide, and 0.05 g. of benzoyl peroxide in 200 ml. of carbon tetrachloride was refluxed with stirring for 30 min. Another 0.05 g. of benzoyl peroxide was added and refluxing was continued for 1.5 hr. The mixture was cooled to 0° and filtered. The residue was washed with 50 ml. of carbon tetrachloride. The combined filtrates were evaporated to

(2) K. H. Hausser, *Z. Naturforsch.*, **14a**, 425 (1959).

(3) Elemental analyses were performed by Berkeley Analytical Laboratories, Berkeley, Calif. Melting points are corrected.

dryness at room temperature on a rotating evaporator. The residue was taken up in the minimum volume of diethyl ether and cooled to 0°. The crystals which formed were filtered, washed with 50:50 diethyl ether-petroleum ether, and dried. The yield was 23 g. (63%), m.p. 121–122°.

*Anal.* Calcd. for  $C_{22}H_{18}Br_2$ : C, 60.82; H, 3.99; Br, 35.19. Found: C, 60.64; H, 3.96; Br, 34.98.

$\alpha$ -(*p*-Isopropenylphenyl)- $\beta$ -diphenylevinyl Bromide (VIII).—A mixture of 150 g. (0.31 mole) of  $\alpha$ -[*p*-(2-bromoisopropyl)phenyl]- $\beta$ -diphenylevinyl bromide and 100 g. (1 mole) of potassium acetate in 1500 ml. of glacial acetic acid was heated on a steam bath for 3 hr. The reaction mixture was cooled to room temperature and poured onto 1 kg. of cracked ice. The solid product was filtered and washed thoroughly with water and acetone. The residue was recrystallized from glacial acetic acid to give 80.5 g. (68.6%) of pale yellow flakes, m.p. 165–166°.

*Anal.* Calcd. for  $C_{23}H_{17}Br$ : C, 74.00; H, 4.59; Br, 21.41. Found: C, 74.23; H, 4.49; Br, 21.14.

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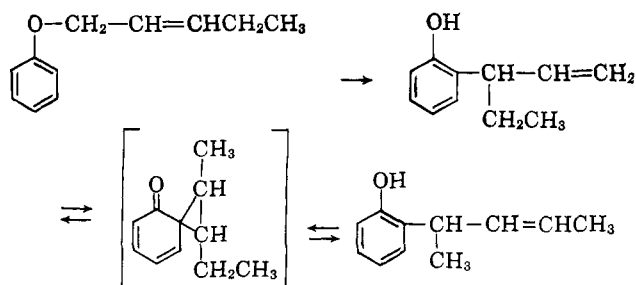
### The Rearrangement of Crotyl- $\delta$ - $C^{14}$ *p*-Carbomethoxyphenyl Ether

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Earlier studies<sup>2</sup> have shown that the thermal rearrangement of  $\gamma$ -alkyl allyl phenyl ethers gives rise to products which would not be expected on the basis of the normal Claisen rearrangement. Unlike the normal rearrangement products, which involve  $\gamma$ -attachment of the substituted allyl group to the aromatic nucleus, these products require an over-all shift of a hydrogen atom from the  $\delta$ - to the  $\alpha$ -position and a  $\beta$ -attachment of the substituted allyl group. Accordingly  $\gamma$ -ethyl allylphenyl ether yielded two products, *o*-( $\alpha$ -ethyl allyl)phenol and *o*-( $\alpha$ - $\gamma$ -dimethyl allyl)phenol. Recently, Marvell, Anderson, and Ong<sup>3</sup> demonstrated that the *o*-( $\alpha$ ,  $\gamma$ -dimethyl allyl)phenol arises from a thermal rearrangement of *o*-( $\alpha$ -ethyl allyl)phenol and that these two products which are obtained by the pyrolysis of  $\gamma$ -ethyl allyl phenyl ether are the result of consecutive rather than concurrent processes. They formulate the transformations as follows.



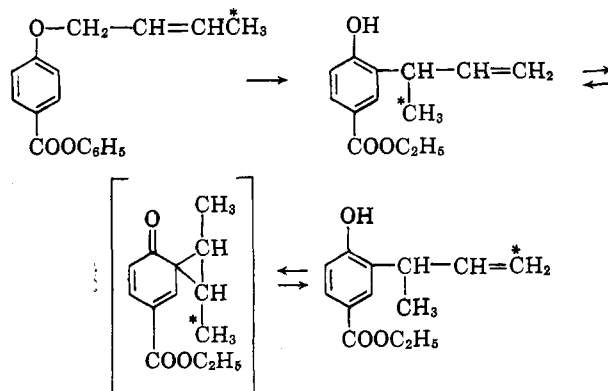
(1) Ph.D., University of Minnesota, 1962.

(2) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936); C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); W. M. Lauer and R. M. Leekley, *J. Am. Chem. Soc.*, **61**, 3043 (1939).

(3) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1110 (1962).

This formulation is consistent with the structural changes observed earlier.

A recent study from this laboratory<sup>4</sup> dealt with the rearrangement of  $C^{14}$ -labeled crotyl *p*-carbomethoxyphenyl ether, and the present work describes its extension in view of these findings. If this pyrolysis is formulated in a similar manner, the intermediate becomes symmetrical.



Heating for a period sufficiently long to reach equilibrium conditions, should give rise to a 50:50 distribution of the radioactivity. This distribution of radioactivity has been observed in samples which have been heated for 280 hours at  $220 \pm 10^\circ$ . Degradation studies have also established the fact that all of the radioactivity resides in the two positions indicated. The oxidation of *o*-( $\alpha$ -methylallyl)-*p*-carboxyanisole- $x-C^{14}$  yielded nonradioactive 4-methoxyisophthalic acid. The transformation of the semicarbazone of  $\alpha$ -(2-methoxy-5-carboxyphenyl)propionaldehyde to (2-methoxy-5-carboxyphenyl)acetone, followed by the conversion of this methyl ketone to iodoform, led to a sample of radioactive iodoform, which, together with that found in dimedone derivative of the formaldehyde produced on ozonolysis, accounted for all of the radioactivity of the starting material.

Similar results have been obtained by Habich, Barner, Roberts, and Schmid.<sup>5</sup> These investigators studied the behavior of crotyl- $\delta-C^{14}$  *p*-methylphenyl ether upon heating. They demonstrated that the radioactivity which initially resided in the position predicted on the basis of a normal Claisen rearrangement was distributed between the methyl and methylene groups upon heating in accordance with the formulation of Marvell, Anderson, and Ong.<sup>3</sup> It is, therefore, clear that the abnormal products which were described earlier result from consecutive and not concurrent processes.

#### Experimental

Crotyl- $\delta-C^{14}$  *p*-carbomethoxyphenyl ether ( $988 \times 10^3$  c.p.m./mmoles) was prepared according to the procedure described by Lauer, *et al.*<sup>4</sup> A number of rearrangements were carried out under the following conditions: (1) heating in a metal bath at  $220 \pm 10^\circ$  after evacuating the container using a heat lamp to prevent the refluxing liquid from crystallizing on the walls of the container; (2) heating in an oven at  $220 \pm 10^\circ$  after evacuating a Pyrex tube to approximately 1 mm. and sealing with a torch; (3) heating in an oven at  $220^\circ \pm 10^\circ$  after repeatedly evacuating and admitting carbon dioxide, the tube being sealed at a pressure

(4) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepins, *ibid.*, **26**, 4785 (1961).

(5) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).