## Triphenyl- and Tetraphenyl-cyclopentadienylidene-pyrans <sup>1</sup> and -thiins

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Triphenyl- and tetraphenyl-diazocyclopentadienes react with 2,6-dimethyl-4H-pyran-4-thione to form cyclopentadienylidenepyrans. A thiin has been similarly prepared from the corresponding thiinthione. The triphenvl derivative does not undergo electrophilic substitution readily. Bases do not attack these pyrans. With acids they form salts, which react with bases either to regenerate the original pyran or to produce a cyclopentadienylidenedihydropyridine.

THE heterocyclic cyclopentadienylidene derivatives of general formula (I) and their ortho-isomers may have aromatic character owing to some contribution from a dipolar canonical form. Examples of such compounds are known wherein  $X = NR^{\frac{1}{2}-4}$  but the only corresponding compounds wherein X = O are either fluorenvlidene <sup>4,5</sup> or indenvlidene <sup>4,6</sup> derivatives.



One way of preparing the fluorenylidene derivatives <sup>5</sup> utilised a reaction first described 7 in 1920, in which a diazo-compound reacts with a thione to give a thiiran which decomposes on heating, with extrusion of sulphur and formation of a double bond.

Cyclopentadienylidenepyrans (II; R = Ph or H, X = O have now been prepared by the reaction of 2,3,4-triphenyl- and 2,3,4,5-tetraphenyl-diazocyclopentadienes with 2,6-dimethyl-4H-pyran-4-thione. A cyclopentadienylidenethiin (II; R = Ph, X = S) has also been prepared from 2,3,4,5-tetraphenyldiazocyclopentadiene and 2,6-dimethyl-4H-thiin-4-thione.

Reaction between the diazo-compound and the pyranthione gave better yields when the reagents were heated in a refluxing solvent whose boiling point was higher than the decomposition temperature of the diazo-compound. Since thermal decomposition of the diazo-compound leads to formation of a carbene, and in view of the isolation of thiirans in earlier work,<sup>5,7</sup> it seems reasonable that the mechanism of the reaction may be as shown. An alternative mechanism involving nucleophilic attack by the cyclopentadienide ring on the thione group is less likely for steric reasons; also, no reaction takes place between the diazo-compound and tropylium ions.

Attempts to carry out a similar reaction using un-

<sup>1</sup> Cf. D. Lloyd and F. I. Wasson, Chem. and Ind., 1963, 1559. <sup>2</sup> F. Kröhnke, K. Ellegast, and E. Bartram, Annalen, 1956, **600**, 176; D. N. Kursanov, N. K. Baranetskaya, and V. N. Setkina, Doklady Akad. Nauk S.S.S.R., 1957, **113**, 116; D. N. Kursanov and N. K. Baranetskaya, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, 1961, 1703; G. V. Boyd, Proc. Chem. Soc., 1960, 253.

<sup>3</sup> J. A. Berson and E. M. Evleth, *Chem. and Ind.*, 1961, 1362; J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Amer. Chem. Soc.*, 1965, **87**, 2887.

substituted diazocyclopentadiene were unsuccessful. Both starting materials could be recovered unchanged but the diazo-compound gradually decomposed to polymeric material having a similar infrared (i.r.) spectrum



to the product obtained when diazocyclopentadiene is heated alone in a solvent or if solutions are kept at room temperature for a few days.

The triphenyl- and tetraphenyl-cyclopentadienylidenepyrans are deep red, while the corresponding thiin is brown. The tetraphenyl derivatives are isoelectronic with a known tetraphenylsesquifulvalene<sup>8</sup> and the ultraviolet (u.v.) spectra are closely similar.

The pyrans are oxidised on being heated to reflux with chromium trioxide in acetic acid, with formation of dimethyl- $\gamma$ -pyrone. On treatment with chlorine the pyran (II; R = Ph, X = O) gave what was apparently a dichloro-addition product, whose u.v. spectrum indicated that the exocyclic double bond had been attacked.

Unlike 2,3,4-triphenyldiazocyclopentadiene,<sup>9</sup> the triphenylcyclopentadienylidenepyran (II; R = H, X =O) did not undergo substitution readily on reaction with N-bromosuccinimide or with mercuric acetate. It did not couple with a diazonium salt.

The diazo-compound undergoes rapid hydrogen-deuterium exchange in deuteriotrifluoroacetic acid, but no such exchange takes place in the case of the pyran,

<sup>8</sup> H. Prinzbach, Angew. Chem., 1961, **73**, 169.
<sup>9</sup> D. Lloyd and F. I. Wasson, J. Chem. Soc. (C), 1966, 408.

<sup>&</sup>lt;sup>4</sup> G. V. Boyd and L. M. Jackman, J. Chem. Soc., 1963, 548. <sup>5</sup> A. Schönberg, M. Elkaschef, M. Nossier, and M. M. Sidky, Amer. Chem. Soc., 1958, 80, 6312; A. Schönberg and M. M. Sidky, ibid., 1959, 81, 2259.

<sup>&</sup>lt;sup>6</sup> G. V. Boyd, Proc. Chem. Soc., 1959, 93.

<sup>&</sup>lt;sup>7</sup> H. Staudinger and J. Siegwart, Helv. Chim. Acta, 1920, 3, 833.

indicating that the cyclopentadienylpyrylium salt so formed is not in equilibrium in acid solution with any appreciable amount of the unprotonated form.

Whereas pyrones and pyrylium salts are in general readily attacked by bases, the present cyclopentadienylidenepyrans are quite unaffected, and have been recovered almost quantitatively after treatment with ethanolic sodium hydroxide or benzylamine. No reaction took place with ammonia or with potassium hydrogen sulphide. Reactions of bases with pyrones or pyrylium salts are assumed to involve the initial formation of a pseudobase. In this case the equilibrium

Initial compound  $\Longrightarrow$  Pseudobase [(III)  $\Longrightarrow$  (IV)]

may well lie entirely on the side of (III), since the conversion of (III) into (IV) involves formation of a



cyclopentadienide anion and this is not normally achieved by any of the bases in question except in the case of cyclopentadienide anions having strongly electron-withdrawing substituent groups. Reactions involving such a pseudobase as intermediate are therefore unlikely.

On addition of perchloric acid to an ethereal suspension of the cyclopentadienylidenepyran the latter is protonated and an orange precipitate of cyclopentadienylpyrylium perchlorate is formed. These salts are indefinitely stable in air. On treatment with alkali, or even on boiling in ethanol, the pyran is regenerated. The corresponding sulphates are less stable and are hygroscopic.

In the case of cyclopentadienylidenedihydropyridines, derivatives of (I; X = NR), the n.m.r. spectra of their acid salts suggest that protonation takes place at either the 2- or 3-position of the five-membered ring, producing two distinct salts.<sup>4</sup> Their ortho-isomers similarly give rise to two protonation products.<sup>3</sup> In neither case was there any evidence of protonation at the 1-position; this will not be favoured since it would lead to interruption of the conjugation between the two halves of the molecule.

In the case of the cyclopentadienylidenepyrans (II; R = H or Ph, X = O), their n.m.r. spectra in trifluoroacetic acid show that only one conjugate acid is formed in either case. In the case of the triphenyl derivative there are signals at  $\tau 2.86$ , 5.67, and 7.45, equivalent to 17, 2, and 6 protons, respectively. The first and last of these signals are due, respectively, to the protons attached to the phenyl and pyrylium rings and to those of the methyl groups. Since there is only one other signal the remaining hydrogen atoms must be equivalent, *i.e.*, the proton from the acid must have attacked the 5-position, forming the salt (V). In deuteriotrifluoroacetic acid, the spectrum is the same save that



the middle signal is now equivalent to only one hydrogen atom. The retention of this signal in the deuterio-acid shows that ready hydrogen-deuterium exchange does not take place, suggesting that the conjugate acid does not dissociate readily (cf. ref. 9). The protonated salts have maxima in their u.v. spectra at longer wavelengths than the parent pyrans; the same applies to the thiin (II; R = Ph, X = S).

These cyclopentadienylpyrylium salts will not react as dienes or as dienophiles in Diels-Alder reactions, presumably because of the conjugation of the diene system with the pyrylium ring.

On treatment with bases the salts are either (a)reconverted into cyclopentadienylidenepyrans or (b)converted into cyclopentadienylidenedihydropyridines. The course which the reaction follows correlates with the base strength of the reagent used. Non-amines, and amines having  $pK_b < ca. 5$  or > ca. 10 regenerate the pyran, while amines having  $pK_b$  between ca. 5-10 react to form pyridine derivatives. Thus, ammonia  $(pK_b 4.75)$  diethylamine (2.9), isopropylamine (3.5), p-aminobenzoic acid (12.0), and p-nitroaniline (13.0), follow course (a) whereas benzylamine (5.2), p-toluidine (9.0), and aniline (9.3) follow course (b). Phenylhydrazine (8.8) and N-methylphenylhydrazine also follow course (b). This variation can be rationalised in terms of the base strength and nucleophilicity of the reagents. Strong bases remove a proton at once and completely from the salt. With amines of intermediate basicity an equilibrium is produced between pyran and salt and the latter is subject to nucleophilic attack by the amine. In the case of p-aminobenzoic acid and p-nitroaniline their nucleophilicity is so low that the only reaction in which they participate is to assist in the removal of a proton from the pyrylium salt. These schemes can be summarised:

$$(PLH^+ = Pyrylium \ salt; \ PL = pyran;$$
  
 $PY = dihydropyridine; \ B = base)$ 

Strong bases

Intermediate strength bases

$$PY \longleftarrow PLH^+ + B \longrightarrow PL + BH^+$$

Weak bases and nucleophiles

The cyclopentadienylidenedihydropyridines formed are, like the pyrans, hybrids of covalent and dipolar forms [cf. (I; X = NR)]. In this case, in contrast to the corresponding pyrans and thiin, the u.v. spectra show a hypsochromic shift on acidification.

The products obtained from the perchlorate of the pyran (II; R = Ph, X = O) and phenylhydrazine or *N*-methylphenylhydrazine are *N*-phenylamino-derivatives, (II; R = Ph,  $X = N\cdot NHPh$  or  $N\cdot NMePh$ ).

## EXPERIMENTAL

2,6-Dimethyl-4-tetraphenylcyclopentadienylidenepyran.—A solution of 2,3,4,5-tetraphenyldiazocyclopentadiene<sup>9</sup> (0.5 g.) and 2,6-dimethyl-4H-pyran-4-thione (0.2 g.) in purified p-cymene (20 ml.) was heated under reflux gently for 7 hr. Solvent was then removed *in vacuo* and the residue chromatographed on alumina. Elution with benzene–light petroleum (b. p. 60—80°) (7:3) produced a residue which was recrystallised from ethanol-benzene (9:1) to give the deep red *pyran* (0.10 g., 17%), m. p. 267—269°,  $\lambda_{max}$ . 261, 425 mµ ( $\varepsilon$  22,050, 31,700) (Found: C, 90.7; H, 6.1. C<sub>36</sub>H<sub>28</sub>O requires C, 90.8; H, 5.9%). A second component, eluted with benzene, consisted of tetraphenylcyclopentadienone. When *p*-cymene was replaced by solvents of lower boiling point, lower yields of pyran were obtained, *viz.*, mesitylene, 13%; toluene, 9%; benzene, 5.5%.

2,6-Dimethyl-4-2',3',4'-triphenylcyclopentadienylidenepyran.—A solution of 2,3,4-triphenyldiazocyclopentadiene \* (1.5 g.) and 2,6-dimethyl-4H-pyran-4-thione (0.65 g.) in mesitylene (50 ml.) was heated under reflux gently for 6 hr. After removal of the solvent *in vacuo* the residue was chromatographed on alumina. Elution with benzenelight petroleum (b. p. 100—120°) (7:3) produced two bands, the first consisting of unreacted thione. The second band yielded a dark solid, which was recrystallised from ethanolbenzene (9:1) to give red needles of the *pyran* (0.2 g., 10.5%), m. p. 261—262·5°,  $\lambda_{max}$  260, 417 mµ (Found: C, 89·2; H, 5·9.  $C_{30}H_{24}$ O requires C, 90·0; H, 6·0%).

2,6-Dimethyl-4H-thiin-4-thione (cf. ref. 10).—Potassium hydrogen sulphide solution was prepared by saturating an aqueous solution of potassium hydroxide (5.9 g. in 10 ml.) with hydrogen sulphide at 0°. A portion (6 ml.) of this solution was added to a solution of 2,6-dimethyl-4H-pyran-4-thione (1 g.) in boiling ethanol (8 ml.). After heating for 4 min., more sulphide solution (3 ml.) was added and heating was continued for 2 min. On cooling, orange needles separated. Recrystallisation from ethanol gave the thiinthione (0.33 g., 29%), m. p. 116—117°.

2,6-Dimethyl-4-tetraphenylcyclopentadienylidenethiin.—A solution of 2,3,4,5-tetraphenyldiazocyclopentadiene (0.5 g) and the foregoing thiinthione (0.2 g.) in mesitylene (15 ml.) was boiled under reflux for 7 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on alumina. Elution with benzene–light petroleum (b. p. 60—80°) (7:3) gave a first red layer, which yielded brown crystals of the *thiin* (0.17 g., 27%), m. p. 239—241°,  $\lambda_{max}$  270, 473 mµ, in acid solution  $\lambda_{max}$ . 309, 505 mµ (Found: C, 88·7; H, 6·25; S, 7·0. C<sub>36</sub>H<sub>28</sub>S requires C, 87·8; H, 5·7; S, 6·5%).

Attempted Reaction of Diazocyclopentadiene with 2,6-Dimethyl-4H-pyran-4-thione.—A solution of diazocyclopentadiene (1·2 g.) and the thione (1·52 g.) in anhydrous toluene (20 ml.) was heated to reflux. The colour immediately darkened and a brown precipitate slowly formed. This precipitate had m. p.  $>310^{\circ}$  and showed intense carbonyl absorption in its i.r. spectrum. Chromatography of the filtrate (alumina-benzene) yielded unreacted starting materials. The brown product was formed when a solution of diazocyclopentadiene in benzene was boiled under reflux in the absence of thione.

Attempted Reaction of Diazo-compound with Tropylium Perchlorate.—A solution of tetraphenyldiazocyclopentadiene (0.2 g.) and tropylium perchlorate (0.096 g.) in acetic acid (15 ml.) was boiled under reflux for 5 hr. After removal of the solvent, trituration of the brown residue with hot benzene, filtration, and recrystallisation from acetic acid (with charcoal), tropylium perchlorate, m. p. 298—304°, was recovered unchanged (0.085 g., 88%).

Oxidation of the Tetraphenylcyclopentadienylidenepyran.— A solution of the pyran (0.03 g.) and chromium trioxide (0.06 g.) in acetic acid (10 ml.) was boiled under reflux for 1 hr. Water was added, the solution extracted with benzene, and the benzene extract washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent and recrystallisation of the residue from benzene–light petroleum (b. p. 100—120°) gave 2,6-dimethyl- $\gamma$ -pyrone (0.0037 g., 50%), m. p. 132°.

Chlorination of Tetraphenylcyclopentadienylidenepyran.— Chlorine gas was passed through a solution of the pyran (0.05 g.) in dioxan (10 ml.) for 10 min. After removal of most of the solvent *in vacuo*, water was added and the whole extracted with benzene. After drying (Na<sub>2</sub>SO<sub>4</sub>) the benzene was removed leaving a green oil (0.053 g., 91%), which, on solution in ethanol and addition of water, gave yellow crystals, m. p. 97—100°,  $\lambda_{max}$  360 mµ (Found: Cl, 26·1. Calc. for C<sub>36</sub>H<sub>28</sub>Cl<sub>2</sub>O: Cl, 23·0%).

Attempted Substitution of the Triphenylcyclopentadienylidenepyran.—(a) Bromination. N-Bromosuccinimide (0.045 g.) in chloroform (9 ml.) was added to the pyran (0.1 g.) in chloroform (4 ml.). After 30 min. water and ether were added. The organic layer was washed several times with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and solvent removed. Elution of the residue from an alumina column with benzene-light petroleum (b. p. 100—120°) (7:3) gave unchanged pyran and a yellow solid, m. p. 126—129°, which appeared to be a mixture of unchanged pyran and about 20% bromocompound (Found: Br, 3.6. A monobromo-derivative requires 16.7%).

(b) Mercuration. The pyran (0.1 g.) in chloroform was added to mercuric acetate (0.08 g.) in dimethyl sulphoxide (3 ml.). The mixture was kept at 40° for 20 min. and then added to an ice-cold solution of sodium iodide (0.0375 g.)in ethanol (2 ml.), and kept for a further 10 min. at 0°. Water and chloroform were then added, the organic layer was washed with water, dried  $(Na_2SO_4)$ , and the solvent removed leaving a brown solid (0.086 g.), m. p. 211— 235°. Elemental analysis indicated incomplete mercuration.

(c) Diazo-coupling. A solution of the pyran (0.05 g.) in methylene chloride (5 ml.) was added, at 0°, to an excess of benzenediazonium chloride solution buffered to pH  $\sim 6$ , and stirred vigorously for 30 min. 5% Aqueous sodium hydroxide was added, and the organic layer was separated, washed twice with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and solvent removed. Chromatography on alumina [benzene-light petroleum (b. p. 100–120°) (1:1)] gave 0.039 g. (78%) of unreacted pyran.

Attempted Reaction of Tetraphenylcyclopentadienylidenepyran with Bases.—(a) Potassium hydroxide. After several hours' reflux with 5% ethanolic potassium hydroxide the pyran was filtered off unchanged.

(b) Potassium hydrogen sulphide. After a suspension of the pyran had been boiled under reflux in 50% aqueous

solution of the sulphide [potassium hydroxide (5.9 g.) in water (10 ml.) saturated with hydrogen sulphide at  $0^{\circ}$ ], filtration and washing with ethanol left unchanged pyran.

(c) Ammonia. The pyran was recovered unchanged after either being boiled for 3 hr. in ethanol-ammonia  $(d \ 0.88; 1:1)$  or on having ammonia gas passed through a solution in warm t-butyl alcohol.

(d) Benzylamine. A solution of pyran and benzylamine in anhydrous benzene was boiled under reflux for 1 hr.; the pyran was recovered unchanged.

Formation of Salts with Acid.—(a) From tetraphenylcyclopentadienylidenepyran. The pyran (0.05 g.) was suspended in anhydrous ether (7 ml.) and perchloric acid (73%; 2 drops) was added. After 2 hr. at 0°, orange crystals of the *perchlorate* were filtered off and washed with ether (0.057 g., 83%), m. p. 172—174°,  $\lambda_{max}$  256sh, 301, 481 mµ ( $\epsilon$  15,000, 14,700, 29,800) (Found: C, 73.7; H, 5.6; Cl, 6.9. C<sub>36</sub>H<sub>29</sub>ClO<sub>5</sub> requires C, 74.9; H, 5.0; Cl, 6.2%). When a sample of the pyran was kept overnight in ether to which a drop of concentrated sulphuric acid had been added, an orange precipitate formed, but on filtration it became dark and oily. Alkali regenerated the pyran in both cases.

(b) From the triphenylcyclopentadienylidenepyran. The pyran (0.05 g.) was suspended in anhydrous ether (7 ml.) and perchloric acid (73%; 2 drops) was added. After being kept overnight at 0° orange crystals of the perchlorate were filtered off and washed with ether (0.057 g., 90%), m. p. 231–232°,  $\lambda_{max}$  305, 481 mµ (Found: C, 71.5; H, 4.9; Cl, 7.0. C<sub>30</sub>H<sub>25</sub>ClO<sub>5</sub> requires C, 71.9; H, 5.0; Cl, 7.1%). Alkali regenerated the pyran.

Recovery of the Pyran from the Pyrylium Salt.—A suspension of 2,6-dimethyl-4-tetraphenylcyclopentadienylpyrylium perchlorate (0.04 g.) in aqueous sodium hydroxide (10%, 10 ml.) was boiled under reflux for 3 hr. The mixture was cooled, filtered, and washed with water and ethanol, giving the corresponding pyran (0.032 g., 96%), m. p. 266—269°. The pyran was similarly recovered when the pyrylium salt was heated with solutions of potassium hydrogen sulphide, hydrazine hydrate, diethylamine, isopropylamine, ammonia, p-aminobenzoic acid, or p-nitroaniline.

1-Benzyl-1,4-dihydro-2,6-dimethyl-4-tetraphenylcyclopentadienylidenepyridine.—On adding benzylamine (0.06 ml.) to a suspension of 2,6-dimethyl-4-tetraphenylcyclopentadienylpyrylium perchlorate (0.08 g.) in dry benzene (10 ml.) the solid dissolved at once to give a red solution. After 1 hr. under reflux, the solution was cooled, washed with dilute aqueous sodium hydroxide and water, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent removed. The red solid obtained was recrystallised twice from ethanol, in which it formed a redgreen dichroic solution, to give deep red crystals of the dihydropyridine (0.045 g., 49%), m. p. 217—220°,  $\lambda_{max}$ . 262, 289, 469 mµ ( $\varepsilon$  17,300, 17,300, 30,950),  $\lambda_{max}$  in acid solution 262sh, 413 mµ ( $\varepsilon$  16,400, 15,100) (Found: N, 2.4. C<sub>43</sub>H<sub>35</sub>N requires N, 2.5%).

1,4-Dihydro-2,6-dimethyl-4-tetraphenylcyclopentadienylidene-1-p-tolylpyridine.—Prepared as the 1-benzyl analogue from the pyrylium salt (0.075 g.) and p-toluidine (0.03 g.) this dihydropyridine formed dark red needles, (from ethanol) (0.022 g., 25%), m. p. 262—264°,  $\lambda_{max}$  262, 425 mµ ( $\epsilon$  23,070, 32,450),  $\lambda_{max}$  in acid solution, 263, 389 mµ ( $\epsilon$  14,060, 28,600) (Found: N, 2.7%).

1,4-Dihydro-2,6-dimethyl-1-phenylamino-4-tetraphenylcyclopentadienylidenepyridine and its Perchlorate.—Phenylhydrazine (0.03 ml.) was added to a suspension of 2,6-dimethyl-4-tetraphenylcyclopentadienylpyrylium perchlorate (0.055 g.) in dry benzene (7 ml.) and the whole heated briefly to reflux. A yellow precipitate of the *perchlorate* was filtered off and washed with benzene (0.0653 g., 89%), m. p. 200—201°,  $\lambda_{max}$  262, 427 mµ ( $\varepsilon$  16,800, 18,750) (Found: Cl, 5.7; N, 4.4. C<sub>42</sub>H<sub>35</sub>ClN<sub>2</sub>O<sub>4</sub> requires Cl, 5.3; N, 4.2%). This perchlorate was shaken with dilute ethanolic potassium hydroxide. Water was then added and the mixture extracted with ether. After washing with water, drying (Na<sub>2</sub>SO<sub>4</sub>), and removal of ether, the dihydropyridine was left as a red solid, m. p. 118—120°,  $\lambda_{max}$  262, 289, 472 mµ ( $\varepsilon$  27,250, 27,350, 49,400).

1,4-Dihydro-2,6-dimethyl-1-(N-methylphenylamino)-4-tetraphenylcyclopentadienylidenepyridine.—N-Methylphenylhydrazine (0.03 ml.) was added to a suspension of 2,6-dimethyl-4-tetraphenylcyclopentadienylpyrylium perchlorate (0.04 g.) in dry benzene (6 ml.) and the mixture was heated briefly to reflux. The resultant solution was cooled, washed with dilute aqueous sodium hydroxide, and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was removed and the residue washed with ethanol to give the dihydropyridine as a brick-red solid (0.0275 g., 57%), m. p. 142—144°,  $\lambda_{max}$ . 263, 288, 474 mµ ( $\varepsilon$  20,450, 21,650, 41,300).  $\lambda_{max}$  in acid solution 263, 433 mµ ( $\varepsilon$ 22,850, 29,500) (Found: C, 88·3; H, 6·2; N, 4·6. C<sub>43</sub>H<sub>36</sub>N<sub>2</sub> requires C, 88·9; H, 6·2; N, 4·8%). This product decomposed slightly in a few days at room temperature.

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<sup>10</sup> F. Arndt, R. Schwarz, C. Martius, and E. Aron, *Rev. Fac. Sci. Univ. Istanbul*, 1948, *A*, **13**, 57 (*Chem. Abs.*, 1948, **42**, **4176**).