gradually with stirring to about 110° in the usual apparatus for simultaneous product take-off, only polymerization took place, a trace of water and unidentified, unpleasant smelling liquid being recovered from the trap.

When chlorohydrin X was treated with potassium hydroxide under the conditions used previously,[6] only an unsaturated alcohol was isolated, b.p. 105–106° (20 mm.), n_D^{24} 1.4807, which could have been either or both of the two possible isomers XIa or b. No further effort was made to clarify this point, however, since no oxetane was obtained.

ROCHESTER 20, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

2,2′,4,4′,6,6′-Hexamethyl-4,4′-bi-4H-pyran[1,2]

KENNETH CONROW[2a] AND PHILLIP C. RADLICK

Received October 17, 1960

The title compound results from the action of strong organic reducing agents on the 2,4,6-trimethylpyrylium cation. It is believed that this is the first example of a bipyran in which the rings are linked by a single bond and the first example of an alkyl-substituted, nonfunctional 4H-pyran.

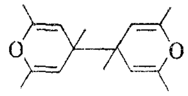
Hafner's elegant preparation of azulene derivatives involves the formation of the seven-membered ring by fusion of a five carbon chain from a pyrylium salt onto the five-membered ring of sodium cyclopentadienide.[3] It was hoped that substitution of the disodium salt of cyclooctatetraene[4] for the cyclopentadienide would not alter the sense of the reaction, so that there would be obtained hydrocarbons with fused seven- and eight-membered rings and extended conjugated double-bond systems.

The reaction between the disodium salt of cyclooctatetraene and 2,4,6-trimethylpyrylium perchlorate was modeled after Hafner's method for the preparation (*ca.* 80%) of the purple 4,6,8-trimethylazulene. The substance isolated (*ca.* 20%) was colorless and proved to have the molecular formula $C_{16}H_{22}O_2$. The possibility that the product arose from the interaction of one dianion of cyclooctatetraene ($C_8H_8{=}$), one trimethylpyrylium cation ($C_8H_{11}O^+$), and one hydronium ion (H_3O^+) (during work-up) was eliminated by the observation that other strong reducing agents, sodium diphenylketyl or the sodium anthracene complex, also act on the trimethylpyrylium ion to give the product (2 and 22% yield, respectively). Thus it is evident that the product arises from the trimethylpyrylium cation by a reductive dimerization process:

$$2C_8H_{11}O^+ + 2e^- = C_{16}H_{22}O_2$$

The best preparative method yet found for the substance (54% yield) involves the use of the potassium salt of cyclooctatetraene with trimethylpyrylium fluoroborate.

The accumulated evidence shows that the dimer has the structure, 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-4H-pyran (I).



I

The substance is very nonpolar; it is eluted from alumina before cyclooctatetraene and before anthracene. It exhibits only tail absorption in the quartz ultraviolet region. Thus there are no conjugated double bonds. A perbenzoic acid titration showed the presence of four double bonds. A C-methyl determination showed the presence of at least five methyl groups.

The most instructive single piece of evidence was the NMR spectrum which showed three sharp singlets at τ values of 5.73, 8.25, and 9.10 with areas in the approximate ratio 4:12:6, respectively. The singlet character of these resonance lines requires that no two carbons which bear hydrogen be linked directly to each other. The resonance occurs at the expected[5] shifts for vinyl hydrogens, allylic hydrogens and methyl hydrogens on saturated carbon, except that the vinyl hydrogens absorb at somewhat higher field than usual, probably because they are well shielded by adjacent methyl groups[6] and are vinylogous to the oxygen atom.[7]

During the early stages of the investigation of the structure of this dimer, two misleading results were obtained which considerably impeded our

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(2) Presented at the A.C.S. Southern California Regional Meeting, Dec. 3, 1960.

(2)(a) New address: Department of Chemistry, Kansas State University, Manhattan, Kansas.

(3) K. Hafner and H. Kaiser, *Ann.*, **618**, 140 (1958).

(4) (a) W. Reppe *et al.*, *Ann.*, **560**, 15 (1948); (b) See T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960); *J. Chem. Phys.*, **32**, 1873 (1960) for a description of recent evidence about the structure of this dianion and references to earlier investigations.

(5) G. V. D. Tiers, Minnesota Mining and Manufacturing Co. Handy Pocket Guide to Characteristic Nuclear Resonance Shielding Values, τ, for Hydrogen Bonded to Carbon.

(6) N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959); esp. Fig. 4 and p. 69.

progress toward elucidation of the correct structure. One was the observation of a strong absorption in the infrared at 1705 cm.$^{-1}$ which we took to be indicative of a ketonic function. Secondly, catalytic hydrogenation in glacial acetic acid with perchloric acid over platinum gave an uptake of about three moles of hydrogen and led to the belief that the dimer had three carbon-carbon double bonds. (The crude hydrogenation product was ketonic, not hydroxylic.)

Closer scrutiny has given evidence that these deductions were erroneous. Attempts to obtain confirmatory evidence for the ketonic function by means of the formation of derivatives (oxime, 2,4-dinitrophenylhydrazone, semicarbazone, α-benzylidene derivative), oxidation (sodium hypoiodite), and reduction (sodium borohydride and lithium aluminum hydride) all failed. The fact that I was recovered unchanged from the basic reaction media (the last four cases) indicates clearly that there is *no* ketone function in the molecule. Thus we are forced to ascribe the absorption at 1705 cm.$^{-1}$ to the enol ether groups of the 4-H-pyran skeleton.

Unfortunately, the literature does not appear to record the infrared spectra of any close models. However, one can make a rough prediction of the enol ether absorption in I if one assumes that the effect of substituents in an enol ether absorption is parallel to the effect of substituents in an ester carbonyl absorption. It is known that formates absorb near 1723 cm.$^{-1}$ and acetates near 1740 cm.$^{-1}$ and that ethyl acetate absorbs at 1740 cm.$^{-1}$ and vinyl acetate at 1776 cm.$^{-1}$[8] Thus substitution of methyl for hydrogen on the carbonyl raises the absorption by 17 cm.$^{-1}$ and introduction of a double bond in the alcohol portion of the ester raises the absorption by 36 cm.$^{-1}$ Under the assumption, and since a number of dihydropyrans with hydrogen on the 2-position absorb near 1650 cm.$^{-1}$,[9] one would predict that a 2-methyl-4-H-pyran would absorb at $1650 + 17 + 36 = 1703$ cm.$^{-1}$[10]

In an effort to obtain a more closely related model compound, 2,4,4,6-tetraphenyl-4H-pyran, the only nonfunctional uncondensed pyran which appears to have been reported,[11] was prepared and found to absorb at 1675 cm.$^{-1}$ While there does not seem to be a convenient way of estimating the amount of lowering of the enol ether absorption frequency by the phenyl substituents on the basis of spectra which appear in the literature, it is clear that an alkyl substituted analog will absorb at higher frequency than this phenyl substituted model.

While these observations cannot be reasonably adduced in direct support of structure I, they do at least indicate that I will absorb at higher frequency than the available model compounds and thus provide permissive evidence for this formulation.

An estimation of the number of double bonds by means of perbenzoic acid indicated, as mentioned above, that there are actually four double bonds in the molecule I. Apparently, the misleading results from catalytic hydrogenation are due to acid catalyzed opening of enol ether functions at least to some extent to give ketonic compounds which resisted further hydrogenation, thus accounting for less than theoretical uptake. The crude hydrogenation product does show strong absorption in the 1700–1710 cm.$^{-1}$ region expected for saturated ketones. Attempts to effect hydrogenation in neutral ethanol or ethyl acetate failed. Attempts at the acid hydrolysis of the enol ether groups gave intractable, easily polymerized oils which gave intractable mixtures of 2,4-dinitrophenylhydrazones. This behavior is not surprising, since the anticipated tetraketone would be capable of a great variety of intra- and intermolecular condensation reactions.

However, when the acid hydrolysis mixtures were treated with base while still fairly dilute, it was possible to isolate various products which appear to have arisen by intramolecular condensation reactions. Four such products were isolated in the pure state and characterized by means of their melting point, analyses, infrared and ultraviolet spectra. Since one can draw over two hundred different compounds (counting stereoisomers) containing only 5-, 6-, and 7-membered rings which could logically arise from the intermediate tetraketone *via* intramolecular aldol reactions, Michael additions, ketalizations and the like, we have made no attempt to pursue the characterization of these substances further.

Attempts to produce other examples of 2,4,4,6-tetraalkyl-4H-pyrans by the reaction of trimethylpyrylium perchlorate with organometallic com-

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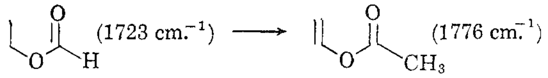
(7) G. V. D. Tiers, Minnesota Mining and Manufacturing Co. N.M.R. Summary, gives the τ value for the corresponding hydrogen in dihydropyran as 5.46, which is to be compared with a value of 4.7 for ordinary disubstituted olefins.[5] The only other possible type of hydrogen which absorbs in this region is that α to an ether oxygen, but all mechanistically reasonable products of this sort would show multiplet absorption bands.

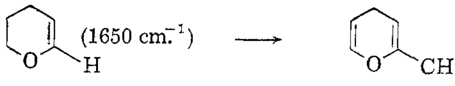
(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Ed., New York, 1958, pp. 179–180, 182.

(9) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5270 (1951); Sadtler Standard Spectra No. 381B, Sadtler Res. Labs., Phila., Pa.

(10) Schematically, the hypothetical process



results in an increase in carbonyl frequency of 53 cm.$^{-1}$ The analogous process



should result in a similar increase in absorption of the double bond chromophore: $1650 + 53 = 1703$ cm.$^{-1}$

(11) Peres de Carvalho, *Ann. Chim.*, [11] **4**, 449 (1935).

pounds were unavailing. A reaction between 2,4,6-triphenylpyrylium perchlorate and the disodium salt of cyclooctatetraene gave no product analogous to I. Attempts to couple 2,4,6-trimethylpyrylium perchlorate by means of inorganic reducing agents (cuprous chloride, sodium in liquid ammonia or potassium in refluxing tetrahydrofuran) failed.

EXPERIMENTAL[12]

I from trimethylpyrylium perchlorate and disodiocyclooctatetraene. To a well stirred suspension of 3.68 g. of sodium sand (0.16 mole) in 200 ml. of freshly dried tetrahydrofuran in a 1-l. flask equipped with a mercury sealed stirrer, reflux condenser, addition funnel, and a nitrogen inlet, was added 10.0 ml. of cyclooctatetraene (0.08 mole). The mixture was refluxed gently under nitrogen until the sodium had completely dissolved. Two hours usually sufficed; the color of the solution was brown, purple, or orange in different runs. The mixture was cooled to room temperature and 14.72 g. (0.056 mole) of trimethylpyrylium perchlorate[13] added. The color changed to deep red. Most of the tetrahydrofuran was distilled off before the mixture was worked up by the addition of water and extraction with petroleum ether. The orange extracts were dried, concentrated, and chromatographed on alumina. The early pentane fractions were colorless and gave colorless crystals, m.p. 113–118°. Later pentane fractions were yellow and had a strong odor of cyclooctatetraene, but gave rise to additional crystals. Further purification was effected by solution in hot ethanol followed by slow crystallization by removal of the solvent at room temperature, m.p. 120–121.0°. Total yield *ca.* 20%.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00; mol. wt., 246.34. Found: C, 78.34, 78.45; H, 8.81, 8.82; mol. wt., 230 (Rast). C-methyl: 4.26.

Spectral data: Ultraviolet: tail absorption only: $\epsilon_{220\ m\mu}^{95\%\ C_2H_5OH}$ 6300. *Infrared:* ν_{max}^{KBr} 3202w, 2930m, 2895m, 2840w, 1705s, 1660w, 1625w, 1450m, 1430m, 1380s, 1360m, 1330w, 1290s, 1225s, 1155s, 1080m, 1050m, 1040w, 1025m, 1000m, 965m, 910m, 895m, 865m, 805s, 675w. In chloroform solution there are four absorptions of about equal intensity in the carbonyl region: 1705, 1685, 1660, 1645 cm.$^{-1}$ Similar loss of strong singlet in the solid state spectrum and appearance of multiple bands in the solution spectrum occurs in the 1225 and 1155 cm.$^{-1}$ regions.

N.M.R.: Two spectra were taken: one in carbon tetrachloride with tetramethylsilane as internal standard and the other with toluene as an external reference. The τ values calculated from the former spectrum were 5.73, 8.25, and 9.10 while the areas determined with a planimeter were in the ratio 3.2:11.9:6.9 and 4.4:11.7:5.8, respectively. The peaks were sharp, symmetrical singlets with widths at their half-height corresponding to 2.5, 3.7, and 2.2 c.p.s., respectively. Any spin-spin coupling, then, must have J values less than about 2.

I from trimethylpyrylium fluoroborate and dipotassiocyclooctatetraene. To 200 ml. of freshly dried and distilled tetrahydrofuran under nitrogen in a 500-ml. flask equipped with mercury sealed stirrer, reflux condenser, addition funnel, and nitrogen inlet, was added 3.91 g. (0.10 mole) of potassium metal followed by 5.75 g. (0.055 mole) of cyclooctatetraene. A spontaneous exotherm occurred as the potassium dissolved and the solution assumed a deep red orange color. After external heating for a few minutes the potassium had completely dissolved. The mixture was cooled to room temperature and 21.0 g. of trimethylpyrylium fluoborate (0.10 mole) in tetrahydrofuran suspension was added from the addition funnel. A slight exotherm accompanied the formation of a white precipitate and lightening of the red color. The bulk of the tetrahydrofuran was removed by distillation at atmospheric pressure and the residue treated with water and petroleum ether (b.p. 60–70°) The aqueous layer was extracted with three additional portions of petroleum ether, the petroleum ether layers combined, dried over magnesium sulfate, and concentrated *in vacuo.* The residue was dissolved in 60 ml. of hot absolute ethanol and allowed to cool. There crystallized 5.45 g. (22 mmoles, 44%) of material, m.p. 112–116°, after collection and washing with cold 95% ethanol. The mother liquor gave additional crystals on dilution with water which were recrystallized from absolute ethanol to give an additional 1.25 g. (10%), m.p. 110–114°, identical with earlier sample by infrared spectrum.

I from trimethylpyrylium perchlorate and sodium diphenylketyl. To 0.92 g. (40 mmoles) of sodium sand in 100 ml. of tetrahydrofuran under nitrogen was added 7.28 g. (40 mmoles) of benzophenone and the mixture stirred until the sodium had dissolved. Then 3.68 g. (14 mmoles) of trimethylpyrylium perchlorate was washed in with more dry tetrahydrofuran. The mixture was stirred and refluxed an hour during which time the color changed to brown. Tetrahydrofuran was distilled off, water was added, the mixture was extracted with petroleum ether and the extracts dried, concentrated, and chromatographed as before. The first pentane eluate yielded a few mg. (*ca.* 2%) of I, m.p. 117–119°, identical with the earlier sample by mixture melting point and infrared spectra.

I from trimethylpyrylium perchlorate and sodioanthracene. To 0.70 g. of sodium sand (30 mmoles) in 150 ml. of dry tetrahydrofuran was added 5.3 g. (30 mmoles) of anthracene. The mixture was stirred and refluxed under nitrogen until the sodium had dissolved and a deep blue solution was obtained. Trimethyl pyrylium perchlorate (5.2 g., 18 mmoles was added in small portions; the color changed to red. After 20 min. at reflux, most of the tetrahydrofuran was removed by distillation and water was added to the residue. The solid was boiled with 65 ml. of absolute ethanol and filtered while hot. The insoluble material, m.p. 215–217°, was anthracene. A crop of less pure anthracene, m.p. 200–215°, was obtained upon cooling the filtrate. The mother liquor was evaporated to dryness *in vacuo,* taken up in petroleum ether and chromatographed on alumina. The first two pentane fractions yielded 0.48 g. (22%) I, m.p. 115–119° and 108–114°, identical with the earlier sample by mixture melting point and infrared spectra.

Perbenzoic acid oxidation of I. A benzene solution of perbenzoic acid was prepared according to Braun[14] using the modifications of Kolthoff.[15] A 5.03-ml. aliquot of the solution was equivalent to 36.70 ml. of 0.1022*N* sodium thiosulfate solution. A solution of 0.1001 g. (0.406 mmole) of I in 10 ml. of benzene was treated with 5.03 ml. of the perbenzoic acid solution and allowed to stand at 25° for 3 days. Then the excess perbenzoic acid was decomposed with a solution of 3 g. of potassium iodide and 5 ml. of glacial acetic acid in 50 ml. of water and the liberated iodine was found to require 4.92 ml. of the standard thiosulfate solution. Thus, 3.98 moles of perbenzoic acid had reacted with each mole of I.

Catalytic hydrogenation of I. A suspension of 35 mg. of platinum oxide in 25 ml. of glacial acetic acid containing 2 drops of 70% perchloric acid was prereduced before 266.1 mg. (108 mmoles) of I was added. A total of 82.6 ml. of hydrogen was absorbed (27.5°, 747 mm.) during about 4.5

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[12] Spectral determinations were made by Miss Donna Karasek on a Perkin-Elmer model 21 and on a Cary model 11. The values reported for the infrared absorptions are internally consistent, but have not been corrected for machine errors. The microanalyses were done by Miss Heather King. Melting points are corrected.

[13] O. Diels and K. Alder, *Ber.*, **60**, 716 (1927).

[14] G. Braun, *Org. Syntheses*, **Coll. Vol. I,** 431 (1941).

[15] I. M. Kolthoff *et al.*, *J. Polymer Sci.*, **2**, 199 (1947).

hr.; this corresponds to an uptake of 3.06 moles of hydrogen per mole of I. A similar experiment in which the perchloric acid was omitted, resulted in the uptake of 2.79 moles of hydrogen per mole of I during 2 hr. The products were inhomogeneous oils with strong absorption in the infrared at 1700–1710 cm.$^{-1}$

Hydrolysis of I. Two putatively identical hydrolyses were performed. A solution of 1.25 g. (5.0 mmoles) of I, 5.0 ml. of water, and ten drops of concd. perchloric acid in 25 ml. of dioxane was allowed to stand for 3 days. Then 5 ml. of 10% sodium hydroxide solution was added and the mixture heated to reflux for 1 hr. The resulting mixture was poured into ether and water, the water layer acidified, extracted an additional time with ether, and the combined ether layers washed with saturated saline and dried over magnesium sulfate. The ether was removed *in vacuo*, the residue taken up in petroleum ether (60–80°), concentrated, and chromatographed on activated neutral alumina. From the first of the two hydrolyses (done on one-fifth the above scale) two crystalline substances were obtained in about 11 and 6% yields, respectively: A, from the pentane eluates, m.p. 50–60°, a ketone ($\nu_{\max}^{\mathrm{KBr}}$ 1690 cm.$^{-1}$). Vacuum sublimation gave partial separation; the less volatile material formed needles m.p. 69.0–69.5°. Ultraviolet: tail absorption only, $\epsilon_{220}^{95\%\ \mathrm{C_2H_5OH}} \sim 670$. A trace of more volatile material was probably compound C, below.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.60; H, 9.32.

B, from the 1:1 pentane:ether eluates, m.p. 70–85° Two recrystallizations from petroleum ether gave platelets, m.p. 121–123°, a hydroxy ketone ($\nu_{\max}^{\mathrm{KBr}}$ 3400, 1697 cm.$^{-1}$). Ultraviolet: weak absorption only, $\epsilon_{220}^{95\%\ \mathrm{C_2H_5OH}} \sim 530$; $\epsilon_{280}^{95\%\ \mathrm{C_2H_5OH}} \sim 45$.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.88; H, 9.05.

From the second hydrolysis two different crystalline substances were obtained in roughly 10% yield each:

C, from the 4:1 pentane:ether eluates, m.p. 81–82°. Vacuum sublimation gave well formed rhombs, m.p. 82.0–83.5°, a hydroxy (?) ketone [$\nu_{\max}^{\mathrm{KBr}}$ 1690 cm.$^{-1}$, 3400 (weak-water in potassium bromide ?)]. Ultraviolet: tail absorption only, $\epsilon_{220}^{95\%\ \mathrm{C_2H_5OH}} \sim 690$.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.86; H, 9.32.

D, from wet ether eluates, m.p. 80–115°. Sixfold crystallization from petroleum ether gave a very poor recovery of thick needles, m.p. 140–141°, an unsaturated hydroxy ketone ($\nu_{\max}^{\mathrm{KBr}}$ 1638, 3400 cm.$^{-1}$). Ultraviolet: $\lambda_{\max}^{95\%\ \mathrm{C_2H_5OH}}$ 236 mμ (ϵ 9500). The behavior on crystallization made it evident that the crude material contains at least one other substance more soluble in petroleum ether than D which has not been obtained in a pure state.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.92; H, 8.95.

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[CONTRIBUTION FROM RESEARCH LABORATORY, UNION CARBIDE CONSUMER PRODUCTS CO., DIVISION OF UNION CARBIDE CORP.]

Chlorination of Aromatic Hydrocarbons by Cupric Chloride. I. Anthracene

JUDITH C. WARE AND EARL E. BORCHERT

Received July 1, 1960

A study has been made of the reaction of cupric chloride with anthracene to yield 9-chloro- and 9,10-dichloroanthracenes, cuprous chloride and hydrogen chloride. An analogous reaction occurred with cupric bromide. The available evidence is consistent with a polar mechanism. A comparison is made of the reactivity of cupric chloride with that of other metal chlorides, some of which are known to act as chlorinating agents.

Several metal chlorides, among them ferric chloride,[1] antimony pentachloride,[2] and aluminum chloride,[3] can effect chlorination of aromatic hydrocarbons. Considerable evidence has been adduced[1a] to suggest that the reactions proceed by a polar mechanism wherein the metal halide acts as an electrophile. It has been found that cupric chloride also functions as a chlorinating agent, yielding the products to be expected for electrophilic chlorination:

$$\mathrm{Ar{-}H} + 2\,\mathrm{CuCl_2} \longrightarrow \mathrm{Ar{-}Cl} + 2\,\mathrm{CuCl} + 2\,\mathrm{HCl}$$

The results of a study of the scope and nature of the reaction are presented here.

RESULTS AND DISCUSSION

When a mixture of anthracene and anhydrous cupric chloride was heated at 200°, a yellow solid rapidly sublimed out of the reaction vessel. Hydrogen chloride was evolved as well. Investigation showed the yellow material to consist of a mixture of chloroanthracenes.

The nature of the reaction was explored by further experiments with anthracene (I), which was selected because its chlorination products were relatively well characterized and easily separated. 9-Chloroanthracene (II) and 9,10-dichloroanthracene (III) were isolated. The reaction product was treated by removing the solvent, if any, by steam distillation, dissolving the salts in hydrochloric acid, and extracting the residue with benzene. Where a single product was obtained, it was purified by recrystallization and, occasionally, chromatography. If a mixture was obtained, its infrared

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[1] (a) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954) and references cited therein; (b) P. Kovacic, R. W. Stewart, and F. J. Donat, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 71-O.

[2] (a) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. IX, Longmans, Green and Co., New York, N. Y. (1929), p. 489; (b) P. Kovacic and A. K. Sparks, Abstracts of Papers, 136th Meeting of the American Chemical Society, Atlantic City, N. J. (September 1959), p. 23-P.

[3] A. Zinke, F. Funke, and N. Lorber, *Ber.*, **60**, 577 (1927).