

invaluable advice. We are also indebted to Mrs. A. L. Klopfer for much of the experimental work.

Glenn D. Cooper, Harry S. Blanchard
G. F. Endres, Herman Finkbeiner
General Electric Research Laboratory
Schenectady, New York
Received June 1, 1965

The Structure of Acetatopentaamminecobalt(III) in $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)$ ¹

Sir:

The recent suggestion by Fraser² that the bonding of the carboxylato groups in carboxylatopentaamminecobalt(III) complexes is an ionic bidentate linkage with both oxygen atoms equivalent led us to investigate the structure of the acetatopentaamminecobalt(III) complex.

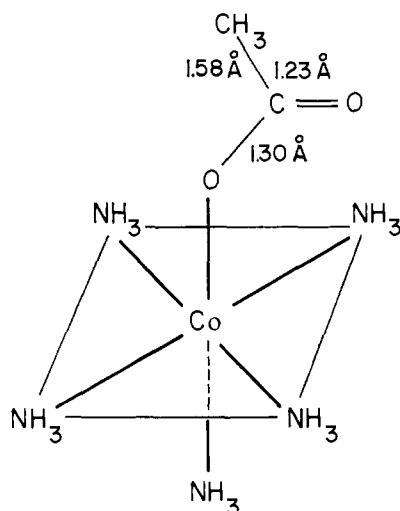


Figure 1. Structure of the acetatopentaamminecobalt(III) ion. The average Co(III)-N distance is 2.00 Å; standard deviations in bond distances \sim 0.02-0.03 Å.

Although the acetate group is known to act as a bidentate ligand in some of its complexes,³ the structure proposed by Fraser contradicts some chemical evidence⁴; also, a seven-coordinate cobalt(III) species seemed unlikely. The crystal studied was $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)$.⁵ The crystal is orthorhombic with cell constants $a = 22.01$, $b = 9.75$, $c = 11.41$ Å.; the space group is Pbcu. The measured density is 1.84 g./cm.³ (the calculated density is 1.83 g./cm.³) which requires eight molecules per unit cell. The intensity data were collected with Mo radiation with a set of balanced filters using a GE XRD5 with a scintillation counter. The residual for the 1143 observed

(1) This research was generously supported by grants from the Public Health Service and A.R.P.A.

(2) R. T. M. Fraser, *Nature*, 202, 691 (1964).

(3) J. van Nieckeck, F. Schoening, and J. Talbot, *Acta Cryst.*, 6, 720 (1953); W. H. Zachariasen and H. A. Plettinger, *ibid.*, 12, 526 (1960).

(4) H. Taube, private communication; this refers to the fact that in the acetatopentaamminecobalt(III) the two oxygen atoms of the acetate group exchange with solvent oxygens at different rates, suggesting a nonequivalence of the oxygen atoms (see R. B. Jordan, Thesis, University of Chicago, 1965).

(5) The crystals were obtained by recrystallizing a sample of the perchlorate salt of the complex, kindly supplied by J. Halpern, in KCl solution with the intention of preparing the dichloride salt; instead, the chloride-perchlorate salt was obtained.

reflections was 14%. The hydrogen atoms were not included in the calculations.

The structure for the acetatopentaamminecobalt(III) is shown in Figure 1. It is clear that the acetate is bonded to the cobalt by a monodentate linkage and that the two oxygen atoms of the acetate are non-equivalent. The bond distances in the structure are similar to those found in related structures.⁶

The carbonyl oxygen atom of the acetate is about equidistant from two ammonia nitrogen atoms with distances that indicate it is participating in hydrogen bonding with these nitrogen atoms.

The carbonate group was recently found to act as a monodentate ligand in the complex, $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \cdot \text{Br} \cdot \text{H}_2\text{O}$.⁷

Acknowledgment. We wish to thank J. Halpern for bringing this problem to our attention.

(6) G. Palenik, *Acta Cryst.*, 17, 360 (1964); Y. Shigeta, Y. Komryama, and H. Kuroya, *Bull. Chem. Soc. Japan*, 63, 1159 (1963).

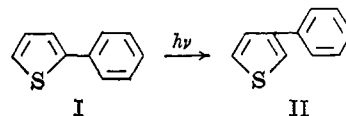
(7) H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 3184 (1965).

Everly B. Fleischer, Rosemarie Frost
Department of Chemistry, University of Chicago
Chicago, Illinois
Received May 20, 1965

The Photochemical Rearrangement of Arylthiophenes

Sir:

When 2-phenylthiophene (I) is illuminated with ultraviolet light for 38 hr. at 80° in benzene solution, 3-phenylthiophene (II) is formed in good yield.



Thus when 98 mg. of 2-phenylthiophene, m.p. 34.5-35°,¹ in 87 g. of benzene to which 6.5 g. of crystallized sodium thiosulfate was added was irradiated with a Hanau S-81² mercury high-pressure lamp and the reaction monitored using quantitative vapor phase chromatography,³ nearly all of the 2-phenylthiophene had disappeared after 38-hr. irradiation, while about 40 mg. of 3-phenylthiophene was formed. Preparative v.p.c. then enabled the isolation of the major component 3-phenylthiophene, m.p. 90-91°, mixture melting point undepressed; infrared and ultraviolet spectra are identical with those of authentic 3-phenylthiophene.⁴

(1) The substance was made by the method of J. L. Melles and H. J. Backer, *Rec. trav. chim.*, 72, 314 (1953); melting points: A. S. Brown and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 59, 1293 (1948); *Chem. Abstr.*, 43, 2614 (1949); infrared spectra: A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.*, 3500 (1959); J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, 12, 773 (1958); ultraviolet spectrum: L. Bruzzi, J. Degani, and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, 19, 40 (1961).

(2) A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Vienna, 1958, p. 126.

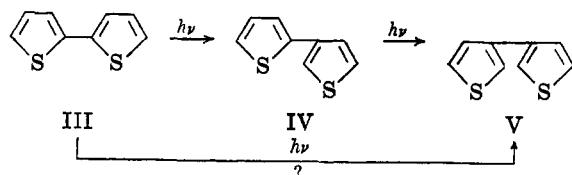
(3) F. & M. Model 810 apparatus with flame ionization detection; immobile phase diethylene glycol succinate (LAC-728); column temperature 190°, using He as carrier gas (60 ml./min.).

(4) Synthesis and melting point: J. L. Melles and H. J. Backer, *Rec. trav. chim.*, 72, 491 (1953); infrared spectrum: H. Rosatzin, *Spectrochim. Acta*, 19, 1107 (1963); J. Degani, M. Pallotti, and A. Tundo, *Ann. Chim. (Rome)*, 51, 434 (1961); ultraviolet spectrum: see Bruzzi, *et al.*¹

Similarly, when 2,2'-dithienyl (III) was irradiated in benzene at 60° for 10 hr. 2,3'-dithienyl (IV) and 3,3'-dithienyl (V) were formed.

The isomer ratio as determined by v.p.c.⁵ was found to be III:IV:V = 25:2:1.

When 2,3'-dithienyl was irradiated in benzene solution, 3,3'-dithienyl was formed.⁶



Irradiation of 3-phenylthiophene and 3,3'-dithienyl in benzene solution caused decomposition, while thus far no isomers have been detected.

Additional evidence for these rearrangements was obtained by measurement of the phosphorescence spectra⁷ of 2- and 3-phenylthiophene and also that of an irradiated sample of 2-phenylthiophene (see Table I).

Table I. Phosphorescence Spectra of 2- and 3-Phenylthiophene

Substance	λ_{\max} , Å.	Decay times, msec.	Rel. intensity
2-Phenylthiophene	5400 \pm 50	20	1
3-Phenylthiophene	4900 \pm 50	300	ca. 13

Figure 1 (upper and middle) shows the phosphorescence spectra of 2- and 3-phenylthiophene in a 2-propanol glass at 77°K. The carefully purified 2-propanol showed no phosphorescence in the region measured.

Figure 1 (lower) shows the phosphorescence spectrum at 77°K. when a solution of 2-phenylthiophene in 2-propanol (10^{-3} M) was irradiated for 1 min. at room temperature using a water-cooled Philips SP-500 super high-pressure mercury arc. The appearance of the 3-phenylthiophene band at λ_{\max} 4900 Å. is clearly evident, while the intensity increase is in accord with the appearance of the 3-isomer. The shoulder at λ 4300 Å. is probably due to decomposition products of 2- and 3-phenylthiophene. This rearrangement was first observed while we were performing photolytic arylation reactions using iodothiophenes as a radical source.⁸

(5) We used a diethylene glycol succinate (LAC-728) column at 190° with He as carrier gas (60 ml./min.) and found a better separation for the compounds under investigation with this column than with a carbowax column as described by S. Berk, *J. Chromatog.*, **15**, 540 (1964). For detection of 2- and 3-phenylthiophenes in mixtures of dithienyls we operated the column at 130° with the same flow. No phenylthiophenes could be detected, which gives support to the hypothesis that the isomerization is not intermolecular.

(6) 2,2'-Dithienyl was not found, but is not excluded because these experiments were carried out with less than 1 mg. of dithienyl.

(7) The phosphorescence spectrophotometer was designed and built by Dr. G. T. Pott, Department of Physical Chemistry of this university. An Osram xenon lamp was used as a light source with a double monochromator, Leiss type with quartz prisms. The detection system consists of a photomultiplier RCA 1 P 28 the signal is amplified by a Philips GM 6020 electronic voltmeter and recorded by a Varian G 14 recorder. Decay times were measured with a Tektronics oscilloscope. A liquid filter between lamp and sample transmits only light between 2600 and 3200 Å.

(8) These synthetic experiments will be published in a subsequent paper. Similar arylations have been reported first by W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961), and more recently by C. E. Griffin and K. R. Martin, *Chem. Commun.* (London), 154 (1965).

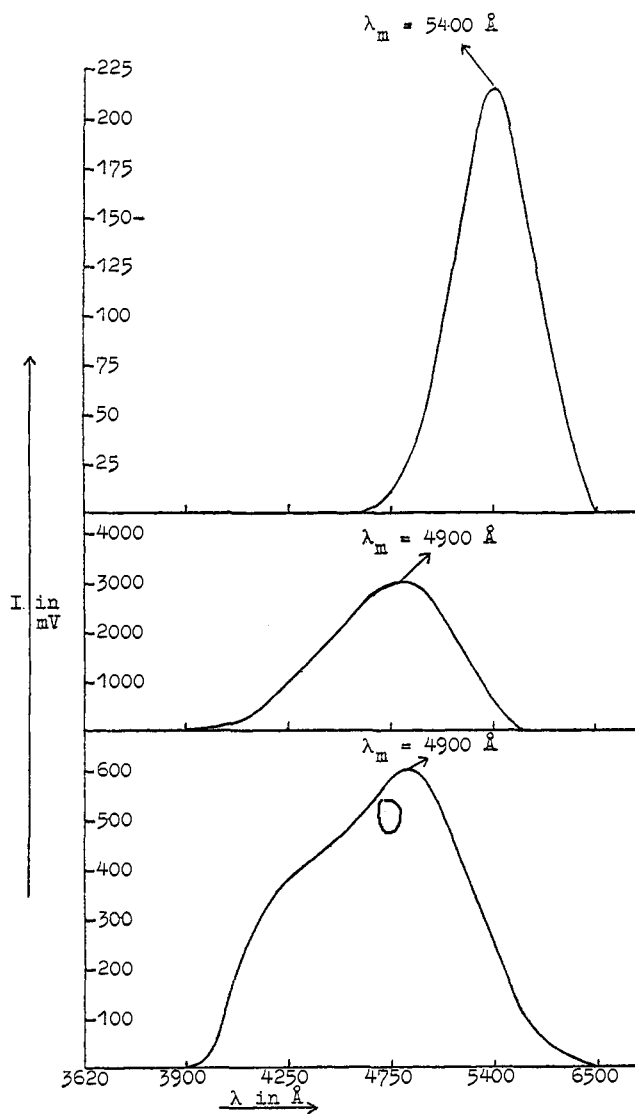


Figure 1.

In view of the recent proposals and evidence⁹⁻¹² for Dewar and Ladenburg intermediates in aromatic rearrangements a similar mechanism for our rearrangement is a preceded interpretation among several alternatives.¹³

(9) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962); K. Kirk, Ph.D. Thesis, University of Wisconsin, 1963. van Tamelen and his students were the first to observe the formation of ground-state Dewar benzene as well as the photoinduced alkyl migration in the benzene series.

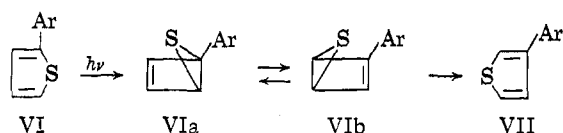
(10) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964); A. W. Burgstahler and P. Chien, *ibid.*, **86**, 2940 (1964); L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965); E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(11) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem.*, **76**, 922 (1964), report nonbenzenoid structures formed directly from acetylene precursors.

(12) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964), report an indazole rearrangement which may proceed by a similar mechanism.

(13) If this hypothesis should be correct the consequences are many. Extensive scrambling of the carbon atoms in thiophenes might be expected upon illumination. Extension of this scheme to other heteroaromatic systems is not excluded. Rearrangements of two substituted heteroaromatics to the 3-isomers under heterolytic conditions are reported,¹⁴ but to our knowledge photochemical rearrangements of this type have not been reported previously.³

(14) S. Gronowitz and P. Moses, *Acta Chem. Scand.*, **16**, 155 (1962).



Acknowledgment. H. van D. thanks the Royal Dutch Shell Co. for a graduate fellowship. The assistance of Mr. D. A. Wiersma, Department of Physical Chemistry, in measuring the phosphorescence spectra is gratefully acknowledged. Valuable technical assistance was given by Mr. J. Buter.

Hans Wynberg, H. van Driel
 Department of Organic Chemistry
 The University Groningen, The Netherlands
 Received June 11, 1965

Determination of Terminal Sequences in Viral and Ribosomal Ribonucleic Acids

Sir:

The use of alkaline degradation for the determination of the terminal nucleotide in the ribonucleic acid of tobacco mosaic virus has been reported by Sugiyama and Fraenkel-Conrat¹ and by Whitfeld.² The terminal base was obtained as the nucleoside adenosine by the isotope dilution method although it was observed that considerable quantities of the other nucleosides were also formed. The authors suggested that this apparent heterogeneity in the terminal base resulted from phosphate exchange between the nucleoside phosphates and the nucleosides during the degradation. It is now confirmed that at least part of this effect is caused by phosphate exchange between the nucleoside and the nucleoside cyclic phosphates which are intermediates in the alkaline hydrolysis. Furthermore, experiments have been designed to minimize this effect, and the terminal sequences of some viral and ribosomal nucleic acids have been determined. Initially, the following general procedure was developed for the estimation of small amounts of nucleosides in the presence of large quantities of nucleotides in alkaline or enzymic hydrolysates.

The alkaline hydrolysate is neutralized with perchloric acid and cooled to 0°. The supernatant solution is removed from the precipitated potassium perchlorate by centrifugation and concentrated *in vacuo* to 1–2 ml. The solution is separated from further precipitated salt and applied to a DEAE-cellulose column (HCO₃⁻ form, 1.7 × 60 cm.) which has been prewashed with water. The salt precipitates are washed with cold water (3 × 2 ml.) and the washings are concentrated to about 2 ml. and also applied to the column. The nucleotides are retained on the column and, on elution with water at 5–10 ml./hr., the salt (KHCO₃) appears first in the eluate, followed by the nucleosides. Under these conditions the nucleosides are obtained free of both nucleotides and salt and can be directly fractionated by paper electrophoresis in ammonium formate (0.05 M, pH 3.0) and estimated spectrophotometrically. In the case of enzymic hydrolyses the solution is concentrated and added directly to the column. A control experiment, in which a mixture of

one absorbancy unit of each of the four nucleosides was run through this procedure, gave better than 90% recovery.

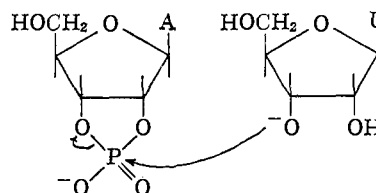
Table I lists the results of alkaline hydrolyses designed to evaluate phosphate exchange reactions between adenosine-2',3' cyclic phosphate and uridine

Table I. Phosphate Exchange between Adenosine-2',3' Cyclic Phosphate (50 mg.) and Uridine

	Uridine, mg.	Time, hr.	Temp., °C.	KOH, N	Volume, ml.	Adenosine formed, % of total nucleoside
I	1	20	37	0.25	10	4.4
II	0	20	37	0.25	10	0
III	1 ^a	20	37	0.25	10	0
IV	1	20	37	0.25	100	2.3
V	1	20	37	0.25	200	1.3
VI	1	15	25	2	10	1.3

^a The uridine was added after the cyclic phosphate had been opened under the conditions given, and the mixture was then kept at 37° for a further 20 hr.

under conditions which would normally result in the complete hydrolysis of ribonucleic acid. The control experiment II shows that no dephosphorylation of the nucleotide takes place in the absence of nucleoside, while experiment III shows that no phosphate exchange occurs after the cyclic phosphate has been opened. Thus it appears that phosphate exchange results from a competition between the 2' or 3' anions of the uridine and the hydroxyl ions in the nucleophilic attack on the cyclic phosphate, yielding uridylyl-(2'(3')→2'(3'))-



adenosine. Attack on the phosphorus by the remaining 2' or 3' anion of the uridine moiety in this dinucleoside phosphate would result in the formation of adenosine and uridine-2',3' cyclic phosphate, the latter being subsequently hydrolyzed to the nucleotide. In the alkaline hydrolysis of ribonucleic acid this method of phosphate exchange is probably supplemented by a mechanistically analogous one involving the attack of the nucleoside anion on some of the unhydrolyzed phosphodiester linkages. With these considerations it is predicted that phosphate exchange should be reduced by lowering the nucleoside concentration relative to the hydroxyl ion concentration. A decrease in the exchange reaction is thus observed under the conditions used in experiments IV, V, and VI.

Table II lists the bases at the 3'-hydroxyl terminus of some ribonucleic acids determined by the methods described above. On alkaline hydrolysis, the RNA of the bacteriophage f2 produced essentially 1 mole equiv. of adenosine together with some cytidine. Adenosine was also obtained by hydrolysis with pancreatic ribonuclease, thus indicating that the penultimate base of f2 RNA is a pyrimidine. A similar result was obtained with the alkaline hydrolysis of the RNA from the bacteriophage MS2, confirming the terminal nucleoside

(1) T. Sugiyama and H. Fraenkel-Conrat, *Proc. Natl. Acad. Sci. U.S.A.*, 47, 1393 (1961).
 (2) P. R. Whitfeld, *J. Biol. Chem.*, 237, 2865 (1962).