trichloromethanesulfonyl chloride, gas chromatographic analysis of the reaction mixtures indicated the presence of only the secondary chloride in the mono-chlorinated products. Distillation of the photo-initiated reaction mixture yielded 0.028 mole of chloroform and 0.026 mole of the secondary chloride (b.p. 56° at 65 mm.).

The high degree of specificity noted in chlorinations with trichloromethanesulfonyl chloride results from the selectivity of the trichloromethyl radical in hydrogen abstraction reactions.[6] Precluding any hydrogen migrations in the free radical which results from the hydrogen abstraction reaction and is subsequently chlorinated in reacting with the chlorinating agent, the site of hydrogen abstraction is the location of the chlorine atom in the reaction product. In chlorinations with chlorine, hydrogen abstraction is performed by a chlorine atom, a free radical more reactive and less selective than a trichloromethyl radical. In the case of sulfuryl chloride chlorinations, the sulfur dioxide complexed chlorine atom, which is less reactive and somewhat more selective than a chlorine atom,[7] is involved in the hydrogen abstraction reaction.

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[6] E. S. Huyser, THIS JOURNAL, **82**, 391 (1960).

[7] G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS
EARL S. HUYSER

RECEIVED AUGUST 19, 1960

THE ABSOLUTE CONFIGURATION OF BIARYLS BY ROTATORY DISPERSION COMPARISON WITH A SESQUITERPENE[1]

Sir:

The extraordinary optical activity of santonide (I) and parasantonide (II) has been the subject of some comment.[2] We now report a striking coincidence: *the rotatory dispersion (RD) curves*[3] *of I and II are virtually superimposable (see Fig. 1)*[4] *on the RD curve of the bridged biphenyl ketone (+)-III,*[5] *while the relative asymmetric disposition of double bond and carbonyl π-electrons in all three compounds (carbon atoms 1–4) is the same.* Since the absolute configurations of I and II are assured,[6] we are led to the conclusion that (+)-III has the (R)-configuration, as shown. *The previously established*[5,7] *absolute configurations of the biaryls have thus been independently corroborated.* A configurational correlation of two different stereoisomeric *types* by the RD-method[8] appears to be without precedent.

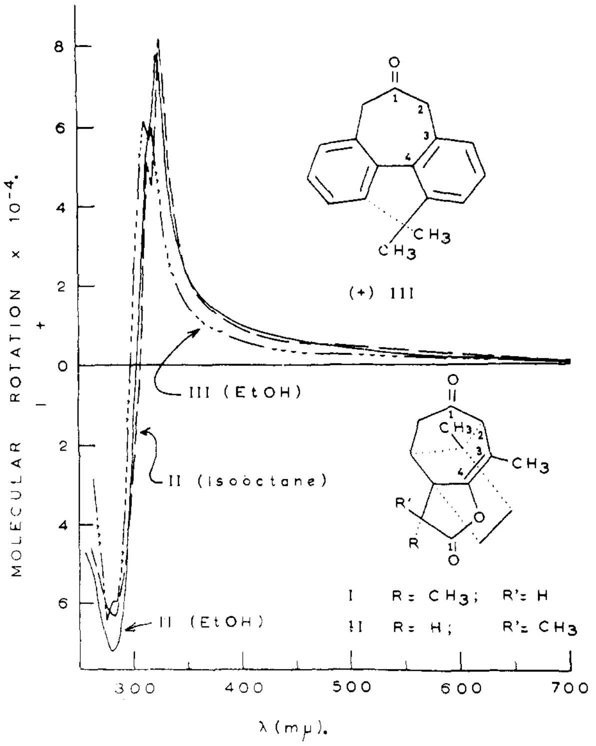

Fig. 1.

We hope to explore the generality of this observation.

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[1] "Configurational Studies in the Biphenyl Series. X." "Optical Rotatory Dispersion Studies. XL." For preceding papers see ref. 5.

[2] R. B. Woodward and E. G. Kovach, THIS JOURNAL, **72**, 1009 (1950); R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[3] S. Mitchell and K. Schwarzwald, *ibid.*, 889 (1939).

[4] The RD curve of parasantonide (II) in ethanol solution measured in our laboratory (Fig. 1) on a sample kindly provided by Prof. R. B. Woodward, is in good agreement with that published earlier (ref. 3). The corresponding curve in isoöctane solution (Fig. 1) is characterized by the same type of fine structure as was recorded (ref. 5) for the isoöctane curve of III and has been attributed to homoconjugation of the carbonyl and benzene π-electrons.

[5] K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg and C. Djerassi, THIS JOURNAL, **82**, 4740 (1960).

[6] R. B. Woodward and P. Yates, *Chem. & Ind.*, 1391 (1954); H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 858 (1956).

[7] K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

[8] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

[9] Fellow of the Alfred P. Sloan Foundation.

[10] Financial support has been provided by the National Cancer Institute (grant No. CRTY-5061) of the National Institutes of Health, U. S. Public Health Service. The rotatory dispersion measurements were made by Mrs. Ruth Record.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.
KURT MISLOW[9]

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA
CARL DJERASSI[10]

RECEIVED JULY 25, 1960

PRODUCTION OF BENZYNE INTERMEDIATES FROM PERCHLORYL AROMATIC COMPOUNDS[1]

Sir:

We have examined the reactions of some perchloryl aromatic compounds with amide ions in liquid ammonia,[2] using anilide ions as a convenient trap for any benzynes produced.[3] Perchlorylbenzene (Ia) undergoes a very vigorous reaction with amide and anilide ions in liquid ammonia at −33°, so vigorous that extensive formation of carbonaceous matter can result unless addition is carefully controlled.[4] The major product iso-

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[1] Presented at the 138th National A.C.S. Meeting, New York, N. Y., Sept. 1960.

[2] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956); J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 611 (1956).

[3] F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

[4] The perchloryl aromatic compound was always added portionwise, and cautiously, to the liquid ammonia medium.

TABLE I

AMIDE REACTIONS

Run	Halide	Moles	Amide	Moles	Halide evolved	Moles	
A	Ib[a]	0.1	$NaNH_2$[b]	0.2	F^-	$<3 \times 10^{-4}$	<3
			$C_6H_5NH_2$	0.1	ClO_3^-	6.6×10^{-2}	66
B	Ia[c]	0.1	$NaNH_2$[b]	0.2	F^-	2.2×10^{-2}	22
	Fluorobenzene	0.1	$C_6H_5NH_2$	0.1	ClO_3^-	8.7×10^{-2}	87
C	Ia[d]	0.05	$NaNH_2$[b]	0.1	F^-	9.5×10^{-4}	2
	Fluorobenzene	0.05	$C_6H_5NH_2$	0.05	ClO_3^-	4.1×10^{-2}	80
D	Fluorobenzene	0.05[a]	$NaNH_2$[b]	0.1	F^-	0	0
			$C_6H_5NH_2$	0.05			
E	Ia[e]	0.025	$NaNH_2$[b]	0.05	Br^-	$<7 \times 10^{-4}$	<3
	Bromobenzene	0.025	$C_6H_5NH_2$	0.025	ClO_3^-	2.0×10^{-2}	80

[a] Diluted with twice its volume of benzene. [b] Sodium in liquid ammonia. [c] With rapid addition of the benzene solution of the aryl halides to the amide ions in liquid ammonia. [d] With slow controlled addition of the benzene solution of the halides to the amide solution. [e] Here, controlled addition of the solution of sodamide and aniline in liquid ammonia to the aryl halides dissolved in liquid ammonia was effected.

lated was triphenylamine and a high yield of chlorate ion was obtained. A similar reaction was run with *p*-fluoroperchlorylbenzene (Ib) wherein the elimination of fluoride ion to form perchlorylbenzyne (IIa) was competitive with loss of chlorate ion, to form fluorobenzyne (IIb). These data and some related runs are summarized in Table I.

The data in Table I, Run A, reveal the dominance of the formation of IIb. As summarized therein we also established (i) that under analogous conditions[5] fluorobenzene is inert (Run D), and (ii) that when a 1:1 mixture of Ia and fluorobenzene is submitted to these reactions with rapid addition of the halides diluted with benzene, a considerable quantity of fluoride ion evolved. That this effect was caused by local heating due to the violence of the aminolysis of Ia was demonstrated when this experiment was repeated (Run C), with every precaution being taken to avoid such heating, and the quantity of fluoride ion then evolved was negligible. The results from Run A also establish that a S_N2 type displacement (toward which Ib is activated)[6] of fluoride ion by anilide ion did not compete with the benzyne process. Finally, the competition between Ia and bromobenzene (Run E), with the complete dominance of Ia, establishes that toward this method of generating benzyne, the sequence of halogenobenzene reactivity is $C_6H_5ClO_3 > C_6H_5Br > C_6H_5Cl > C_6H_5F$.

The Wittig method of producing benzyne, *i.e.*, by the reaction of halogenobenzenes with aryllithium compounds in ether,[7,8] has been shown[9] to involve the reverse of this reactivity sequence, *viz.*, $C_6H_5F > C_6H_5Br > C_6H_5Cl > C_6H_5I$.

Accordingly, the perchloryl aromatic compounds then were treated with aryllithium compounds. Some new perchlorylbenzene derivatives, the *p*-bromo-(Ic) and p-chloro-(Id) compounds were first prepared. When bromobenzene was perchlorylated,[10] the major product was *p*-dibromobenzene, m.p. 84–85° (together with some *p*-chlorobromobenzene) and a 20% yield of Ic, m.p. 93–94°, was obtained. Similarly, perchlorylation of chlorobenzene yielded mainly *p*-dichlorobenzene, m.p. 55–58°, and Id, m.p. 61–62°, was obtained in 15% yield.[11] Some screening experiments were performed first. Thus ethereal solutions of Ia, Ib, or Ic were refluxed with a suspension of lithium for 30 minutes. No reactions were detected. Under similar conditions, Ic did not react with magnesium turnings even with iodine present. The Wittig procedures then were studied.[12] An ethereal solution of phenyllithium reacted very vigorously with Ia producing biphenyl and chlorate ion in high yield.[13] This reaction then was extended to the halogenoperchlorylbenzenes where competitive processes may occur.[14] With Ib, Ic and Id, and phenyllithium in ether the perchloryl group was the exclusive labile fragment, the yields of chlorate ion displaced being 70, 87 and 66%, respectively.[13] When the concentrations of other halides detected were corrected for the bromide ions in the phenyllithium solution,[15] they were negligible.

A further *inter*molecular competitive experiment was run to emphasize this dominance of reaction of the perchloryl moiety. Thus, one mole of phenyllithium in ether was added cautiously to an ethereal solution of one mole of Ia and one

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(5) Generally the additions took 30 minutes, the mixtures were stirred for a further 30 minutes, ammonium chloride was added to quench the amide ions, ether was added and the ammonia was allowed to boil off.

(6) F. L. Scott and R. E. Oesterling, to be published.

(7) G. Wittig and H. Härle, *Liebigs Ann. Chem.*, **623**, 17 (1959), and previous papers.

(8) E. F. Jenny and J. D. Roberts, *Helv. Chim. Acta*, **38**, 1248 (1955).

(9) R. Huisgen and J. Sauer, *Chem. Ber.*, **92**, 192 (1959).

(10) Using our standard method, see C. E. Inman, R. E. Oesterling and E. A. Tyczkowski, THIS JOURNAL, **80**, 5286 (1958).

(11) Compounds Ia, Ib, Ic and Id are shock-sensitive. We recommend care in handling these materials.

(12) These reactions were run under dry nitrogen and involved adding the ethereal phenyllithium solution to the ethereal solution of the perchloryl aromatic compound. During this addition, reaction was brisk enough to maintain the ether at reflux. Subsequently, the mixture was stirred for 30 minutes at ambient temperatures and worked up.

(13) Carbonation of the reaction mixtures prior to work-up failed to yield any carboxylic acid derivatives.

(14) Which substituted benzyne is produced should depend upon the position of initial lithiation, as well as the possibility of halogen metal exchanges. See H. Gilman and J. W. Morton, Jr., *Organic Reactions, VIII*, 258 (1954); R. G. Jones and H. Gilman, *ibid.*, *VI*, 339 (1957).

(15) This was prepared as described by Gilman and Morton (ref. 14), and filtered through glass wool. As thus obtained, it was 1.2 molar in bromide ion.

mole of fluorobenzene, the reaction being quenched while incomplete. The relative yields of chlorate and fluoride ions were as 8:1 (ClO_3^-, *ca.* 32%; $F^- < 4\%$). As is evident from these Wittig reactions the perchlorylbenzenes did not undergo reactivity reversal (relative to the other halogenobenzenes) with change in the mode of benzyne synthesis.

We ascribe the dominance of the perchloryl moiety in these elimination processes to a combination of its high electronegativity[6] (and consequent acidity of proximate aryl hydrogens) and its excellent anionic leaving group ability.[6]

This work was supported in part by the Air Research and Development Command.

PENNSALT CHEMICALS CORP. FRANCIS L. SCOTT
RESEARCH AND DEVELOPMENT DEPT.
WYNDMOOR, PA. ROBERT E. OESTERLING

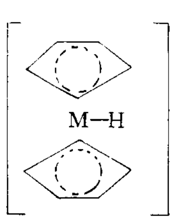
RECEIVED AUGUST 16, 1960

PROTONATION OF METALLOCENES BY STRONG ACIDS. STRUCTURE OF THE CATION

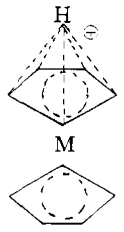
Sir:

Ferrocene recently has been shown to form a stable complex salt of composition ($C_{10}H_{10}Fe \cdot HAlCl_4$) in the presence of aluminum chloride and hydrogen chloride.[1] This finding, together with the suggestion[2] that the transition state for electrophilic substitution of ferrocene, ruthenocene and osmocene may involve initial interaction of the electrophile with the metal atom, prompted us to examine the n.m.r. spectra of these metallocenes in media of high acidity.

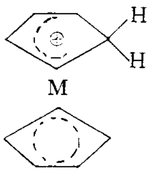
We now wish to report preliminary results of these studies which demonstrate that, in solutions of boron trifluoride hydrate, the cation resulting from protonation of the metallocene possesses structure I. These data are summarized in the table.



I



II



III

FERROCENE

Solvent	Peak position[a]	Relative intensity
$BF_3 \cdot H_2O$	4.99 (sym. doublet; $J = 1.2 \pm 0.2$)[b]	11 ± 2
	12.07 (broad)[b]	1
$BF_3 \cdot H_2O$	5.05 (sym. doublet; $J = 1.3 \pm 0.2$)[c]	15 ± 2
	12.10 (broad)[c]	1
$BF_3 \cdot H_2O$-CF_3CO_2H (1:2)	4.97 (sym. doublet; $J = 1.5 \pm 0.2$)[c]	12.5 ± 2
	11.89	1
$BF_3 \cdot H_2O$-CF_3CO_2H (2:1)	5.02 (sym. doublet; $J = 1.8 \pm 0.2$)[c]	13 ± 2
	11.91	1
CF_3CO_2H	5.33 (singlet)[c]	...
CCl_4	5.958 (singlet)[d]	...
	RUTHENOCENE	
$BF_3 \cdot H_2O$	4.67 (singlet)[c]	16 ± 2
	17.2[c]	1
CCl_4	5.58 (singlet)[c]	...
	OSMOCENE	
$BF_3 \cdot H_2O$	4.88 (singlet)[c]	...
$CDCl_3$	5.29 (singlet)[c]	...

[a] Peak positions are given in ppm. relative to tetramethylsilane having an assigned value of 10 [*cf.* G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)]. Internal standard in acid media, $(CH_3)_3CCO_2H$ ($\tau = 8.77$); in neutral media, $[(CH_3)_3Si]_2O$ ($\tau = 9.95$). [b] Determined at 60 mc. [c] Determined at 40 mc. [d] Value reported by G. V. D. Tiers, abstracts of the 137th Meeting of the American Chemical Society, April 1960, p. 4-O.

The absence of complex unsymmetrical multiplet absorption for the cyclopentadienyl ring protons, together with the appearance of resonance absorption at unusually high magnetic fields are not consistent with a formulation such as III for the protonated metallocenes.[3]

Although the presence of a highly shielded proton may be accounted for in terms of the pi-complex structure II, the apparent magnetic equivalence of protons on each of the cyclopentadienyl rings is not in accord with such a formulation. Symmetrically diprotonated structures of this type are eliminated on the basis of the relative integrated intensities of the magnetically non-equivalent protons.

Structure I for the protonated species is in accord with the appearance of very high field absorption characteristic of a proton bonded directly to the metal atom.[4] The field independent doublet splitting of ring protons in the spectrum of the ferrocene cation readily is assigned to spin coupling of these nuclei with the metal bound proton. The magnitude of this coupling ($J = 1.3 \pm 0.2$ c.p.s.) is similar to that reported by Green, Pratt and Wilkinson for bis-cyclopentadienylrhenium hydride[4] ($J = 1.0_5$ cps.). Furthermore, the magnetic equivalence of all ring protons implies that in the protonated metallocenes, the two cyclopentadienyl rings are relatively free to rotate, as they are in ferrocene.[5]

Ruthenocene is apparently a somewhat weaker base in $BF_3 \cdot H_2O$ than is ferrocene, judging by the relative peak intensities of the high and low field absorptions for the two substances. The absence of spin splitting of ring protons in the spectrum of the ruthenocene cation, as well as the sharp appearance of the high field absorption peak, is attributable to a rapid exchange of the acid proton.[6]

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(1) M. Rosenblum and J. O. Santer, THIS JOURNAL, **81**, 5517 (1959).

(2) J. H. Richards, presented at the 135th Meeting of the American Chemical Society, April 1959; *cf.* abstracts, p. 86-O.

(3) For comparison, *cf.* M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959), for the n.m.r. spectra of $(C_6H_6)(C_5H_5)Co$ and $(C_5H_6)(C_5H_5)Rh$; *cf.* also C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

(4) *Cf.*, for example, J. Chatt and R. G. Hayter, *Proc. Chem. Soc.* 153 (1959); G. Wilkinson, *Angew. Chem.*, 35 (1960); M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(5) Yu. T. Struchkov. *Zhur. Obshchei Khim.*, **27**, 2039 (1957); L. N. Mulay, E. G. Rochow and E. O. Fischer, *J. Inorg. and Nucl. Chem.*, **4**, 231 (1957); M. Rosenblum and R. B. Woodward, THIS JOURNAL, **80**, 5443 (1958).

(6) For a discussion of the dependence of rates of protolysis of amine salts on their basicity, *cf.* A. Lowenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957), and C. G. Swain, J. T. McKnight and V. P. Kreiter, THIS JOURNAL, **79**, 1088 (1957).