at the beginning of the inhibition period and $k_c = k'_{1a}/k_{1a}$.[4]

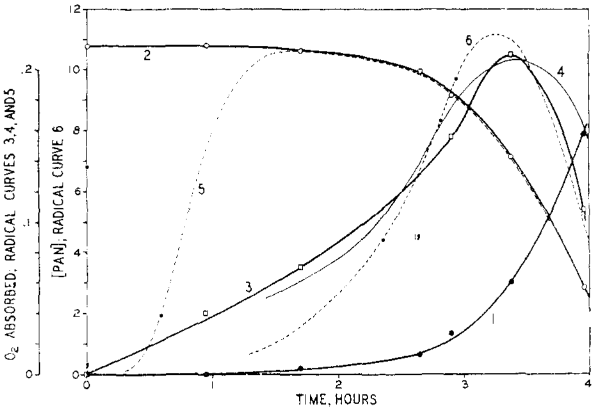
The Boozer and Hammond inhibition processes give

$$[(RO_2ArXH)\cdot] = \left(\frac{K_{1b}}{k'_{1b}}\right)^{1/2} [ArXH]^{1/2} (k_i + k_4[RO_2H])^{1/2} \quad (3)$$

during the inhibition period, where $(k_i + k_4 [RO_2H]) = -\,d[ArXH]/dt$.

We have followed the concentration of a radical formed during the oxidation at 171° of octadecene, inhibited with phenyl-α-naphthylamine (PAN) at 0.0108 *M* initial concentration. The radical concentration was determined by electron paramagnetic resonance measurements[5] made upon samples withdrawn during the course of the oxidation reaction and immediately frozen in liquid nitrogen. The half-life of the radicals at 25° was estimated to be about 30 hours. No radicals were detected in the unoxidized sample, in the inhibitor by itself, or in octadecene oxidized in the absence of inhibitor.

The results of our measurements are shown in the accompanying figure. The radical concentrations observed during the course of the reaction agree approximately with those predicted by the Boozer and Hammond reactions (Equation 2) for $K_{1b}/k'_{1b} = 1.1 \times 10^{-6}$ hour.



Oxidation of octadecene inhibited by 0.108 *M* phenyl-α-naphthylamine (PAN), at 171°: 1, oxygen consumed (moles/liter); 2, [PAN], $M \times 10^3$; 3, observed radical, $M \times 10^4$; 4, calculated radical ($M \times 10^4$), Equation 3, $K_{1b}/k'_{1b} = 1.1 \times 10^{-6}$; 5, calculated radical, Equation 2, $k_c = 500$; 6, calculated radical, Equation 2, $k_c = 7$.

The Kooyman and Bickel reactions, however, require either that the peak radical concentration be 50 times that observed (Curve 6), if the peak is to occur at the time in the reaction at which it is observed to occur, or that the peak occurs much earlier in the reaction and that the shape of the curve (Curve 5) be quite different from that observed, if the observed peak radical concentration is to be matched.

The great stability of the radical at room temperature argues somewhat against the Boozer and Hammond mechanism, because if the radical is formed reversibly, radical decay by $RO_2\cdot + RO_2\cdot$ is possible.

The inhibitor decay curve measured by a fluorescence method and the oxygen absorption curve are acceptable by both mechanisms.

Reaction (1) can also provide the radical concentrations observed if it is assumed that the radical product is destroyed rapidly by some oxidation product, perhaps peroxide, which rises to high concentration near the end of the inhibition period.

Attempts were made to measure concentrations of radicals formed during inhibition periods in octadecene at 171° where the inhibitors were 4-amino-3-pentadecylphenol, di-*t*-butyl-*p*-cresol, and *t*-butylcatechol. No radicals were found. The experiments are being continued at lower temperatures in the hope that increased radical stability will permit detection.

We are indebed to Dr. R. H. Sands and to Varian Associates of Palo Alto, California, for the electron paramagnetic resonance measurements.

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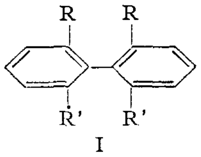
RECEIVED APRIL 4, 1957

THE ABSOLUTE CONFIGURATION OF 6,6'-DINITRO-2,2'-DIPHENIC ACID AND 6,6'-DIMETHYL-2,2'-BIPHENYLDIAMINE

Sir:

Kuhn and Rometsch have assigned[1] the R-configuration to (−)-Ia as a result of calculations based on a theoretical model.[2] We have now obtained evidence directly at variance with the above conclusion.



I

Ia, R = CH_3, R' = NH_2
b, R = COOH, R' = NO_2
c, R = $COOCH_3$, R' = NO_2
d, R = CH_2OH, R' = NO_2
e, R = CH_2Br, R' = NO_2
f, R = CH_3, R' = NO_2

Esterification of (−)-Ib[3] (m.p. 230–233°, $[\alpha]^{23}_D$ −125° (MeOH)) gave (−)-Ic (m.p. 141–142°, $[\alpha]^{28}_D$ −113° (EtOAc)); found: C, 53.6; H, 3.2, N, 8.2), which was reduced to (−)-Id (m.p. 120–121°, $[\alpha]^{20}_D$ −65° (EtOAc)); found: C, 55.5; H, 3.7; N, 9.1) with $LiAlH_4$–$AlCl_3$. Conversion to (−)-Ie (m.p. 172–173°, $[\alpha]^{32}_D$ −8.9 (THF); found: C, 39.3; H, 2.1; N, 6.7) was followed by ring-closure to the iminonitrile (m.p. 295–300° dec., $[\alpha]^{28}_D$ +837° (pyridine); found: C, 60.1; H, 3.7; N, 17.4). Hydrolysis gave DNDBCH-6-one[4] (m.p. 227–229°, $[\alpha]^{25}_D$ +218° (EtOAc); found: C, 61.0; H, 3.8; N, 9.5). Since (+)-DNDBCH-6-one has the S-configuration,[4] the absolute configuration of (−)-Ib is thus established. Ib is of historical interest: it is the first compound[5] known to owe its optical activity to restricted rotation about a single bond.

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(4) Papers 22 (O. L. Harle and J. R. Thomas) and 23 (O. L. Harle) presented at the General Session of the Petroleum Division of the ACS, April 7-12, 1957; kinetic analyses available in Petroleum Division Preprints.

(5) J. E. Wertz, *Chem. Rev.*, **55**, 829-955 (1955).

(1) W. Kuhn and R. Rometsch, *Helv. Chim. Acta*, **27**, 1346 (1944).

(2) Reviewed by W. Kuhn, *Z. Elektrochem.*, **56**, 506 (1952).

(3) A. W. Ingersoll and J. R. Little, THIS JOURNAL, **56**, 2123 (1934).

(4) K. Mislow and P. Newman, *ibid.*, **79**, 1769 (1957).

(5) G. H. Christie and J. Kenner, *J. Chem. Soc.*, 614 (1922).

Reduction of $(-)$-Ie with NaBH$_4$-AlCl$_3$ to $(-)$-If (m.p. 95–97°, $[\alpha]^{27}\mathrm{D}$ $-25°$ (EtOH); found: C, 62.0; H, 4.2; N, 10.3), followed by hydrogenation over Pd/C, afforded $(-)$-Ia (m.p. 153–158°, $[\alpha]^{26}\mathrm{D}$ $-49°$ (EtOH)). The melting point, 232–233°, of the diacetamide, $[\alpha]^{30}\mathrm{D}$ $+134°$ (EtOH), was undepressed by admixture of authentic[6] diacetamide, m.p. 233–235°, $[\alpha]^{26}\mathrm{D}$ $+128°$ (EtOH), prepared from authentic[6] $(-)$-Ia, m.p. 156–158°, $[\alpha]^{24}\mathrm{D}$ $-47°$ (EtOH), $+34°$ (*N* HCl).[7]

$(-)$-Ia and $(+)$-DNDBCH-6-one have thus been correlated *via* $(-)$-Ie; $(-)$-Ia therefore[4] has the S-configuration. It would appear that the assumptions underlying the theoretical treatment[1,2] deserve re-examination.

The absolute configurations of the many common hindered biphenyls related[8] to Ia and Ib will be listed in future publications.

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[6] J. Meisenheimer and M. Höring, *Ber.*, **60**, 1425 (1927).

[7] The sign of rotation of Ia is *p*H dependent (F. A. McGinn, unpublished results).

[8] *Cf.* also K. Mislow, *Trans. N.Y. Acad. Sci.*, [2] **19**, 298 (1957).

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LEWIS ACID CHARACTER OF TELLURIUM HEXAFLUORIDE

Sir:

In a previous communication,[1] the formation of fluorotellurate salts from tellurium hexafluoride and certain alkali metal fluorides was described. We have now found that tellurium hexafluoride will react exothermally with tertiary amines to form stable adducts of the composition $\mathrm{TeF_6 \cdot 2R_3N}$. Analysis of the n-m-r data suggests that geometrical isomers are present in solutions of the trimethylamine complex.

Trimethyl- and triethylamines were added to tellurium hexafluoride in a vacuum system. The trimethylamine adduct was a white solid, but the ethyl analog had a dark color that apparently was due to minor secondary reactions. The pressure–volume relationships indicated a stoichiometry of two molecules of amine for one of the hexafluoride and analysis of the trimethylamine complex confirmed the indicated composition (*Anal.* Calcd. for $\mathrm{TeF_6 \cdot 2N(CH_3)_3}$: C, 20.0; H, 5.04; F, 31.7. Found: C, 19.56; H, 5.10; F, 29.14). Pyridine formed a complex that was highly dissociated at 25°, but amides, ethers and nitriles did not absorb tellurium hexafluoride at this temperature. This low acceptor strength and the previously cited[1] low stability of fluorotellurate salts indicate that tellurium hexafluoride is a relatively weak Lewis acid.

The F^{19} magnetic resonance spectrum of the molten trimethylamine adduct showed only one sharp peak; amine exchange through simple dissociation of the complex was therefore indicated. A dimethylformamide solution of the trimethylamine adduct gave a single broad resonance at 25°, and at higher temperatures, the peak sharpened and shifted in the direction of the tellurium hexafluoride resonance. The amide solution was cooled to a glass that at $\sim -180°$ displayed three broad resonances of approximate intensities 1:1:0.4. On warming above $-180°$, these three peaks broadened rapidly (but at different rates) and finally merged into a single peak. It should be noted that the weak doublet due to spin–spin coupling of fluorine with the Te^{125} isotope persisted at 25° (masked at low temperatures by the broad resonances), and therefore no fluorine exchange was taking place in this system.

The n-m-r data are consistent with the behavior of an octacovalent complex which has geometrical isomers and which undergoes amine exchange through simple dissociation of the complex. At $\sim -180°$, the three fluorine resonances may be ascribed to the three possible isomers. On steric grounds, the two peaks of relative intensity 1 probably arise from the 1,8- and 1,3-isomers, and the peak of relative intensity 0.4 from the 1,2-isomer. Above $\sim -180°$, slight dissociation of the complexes leads to amine exchange and this occurs at different rates for the three isomers. At higher temperatures the three isomers are indistinguishable in the n-m-r spectrum because of fast amine exchange. At temperatures above 25°, the complex is highly dissociated in solution and the position of resonance is a measure of the equilibrium constant for the dissociation. Without supporting data, these conclusions cannot be considered rigorously established. Unfortunately, the rapid amine exchange will not permit isolation of the postulated isomers by conventional techniques.

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RECEIVED APRIL 15, 1957

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[1] E. L. Muetterties, THIS JOURNAL, **79**, 1004 (1957).

A CRYSTALLIZABLE ORGANOMETALLIC COMPLEX CONTAINING TITANIUM AND ALUMINUM

Sir:

Following our previous researches[1] concerning the nature of the catalytic agent promoting the α-olefins polymerization, we have isolated a crystallizable compound containing titanium, aluminum and organometallic bonds, which causes the polymerization of ethylene.

By treating 0.01 mole of bis-(cyclopentadienyl)-titanium dichloride[2] suspended in 50 ml. of *n*-heptane with 0.025 mole of triethylaluminum at 70°, in the absence of air and of moisture, a slow gas evolution takes place, the titanium compound is dissolved and the solution becomes dark blue. By cooling the solution at $-50°$, a blue crystalline solid has been obtained in good yield.

The macroscopic blue needles of the compound, recrystallized four times from *n*-heptane, melt at 126–130° without appreciable decomposition.

---

[1] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *La Chimica e l'Industria*, **38**, 124 (1956); G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *ibid.*, **39**, 19 (1957).

[2] G. Wilkinson and G. M. Birmigam, THIS JOURNAL, **76**, 4281 (1954).