The blue compound contains titanium, aluminum, chlorine and organic groups; from the elementary quantitative analysis a ratio Ti:Al:Cl = 1:1:2 has been found.

The values 331 and 339 have been calculated for the molecular weight of the blue compound from two different cryoscopic measurements in benzene.

By treating the blue product with 2-ethylhexanol, ethane is evolved; a quantitative gas volumetric determination shows that two moles of ethane are evolved per mole of compound.

By treating the product with anhydrous hydrochloric acid in ether solution bis-(cyclopentadienyl)-titanium dichloride is formed in almost quantitative yield (more than 90%).

The analytical data and the chemical behavior agree very well with a formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, as shown in the table for $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

	Calcd.	Found	
Cl, %	21.22	21.02[3]	20.78[4]
Al, %	8.073	7.92	7.90[3]
Ti, %	14.33	14.34	14.55[3]
$-C_2H_5$, %	17.40	16.07	17.67[5]
Mol. weight	334	331	339[6]

It seems probable that, in the complex, both C_5H_5- groups are bound to the titanium atom and that both C_2H_5- groups are bound to the aluminum atom.

By polymerizing ethylene in heptane solution in the presence of 0.6 g. of the Ti-Al complex at 40 atm. and 95° after a reaction time of 20 hours, 8.4 g. of white polymer has been obtained, which has been fractionated by boiling solvent extraction (acetone extractable fraction 10.1%; ether extractable fraction 1.8%, carbon tetrachloride extractable fraction 17.20%, residue 70.9% having intrinsic viscosity in tetralin at 135° = 1.55 × 100 ml./g.).

As it is reported in the next table, $(C_5H_5)_2TiCl_2$ alone is completely inactive for the ethylene polymerization; $Al(C_2H_5)_3$, accordingly with previously published data,[7] does not give solid polyethylene in the reaction conditions, but only low molecular weight oily polymers. Comparative experiments were carried out at 95° and 40 atm.

Soluble catalyst Type	Soluble catalyst Moles	Solvent Type	Solvent Cc.	Reaction time, hours	Crystalline polyethylene, g.	Oily polymers, g.
$(C_5H_5)_2TiCl_2$	0.005	Benzene	100	20	0	0
$Al(C_2H_5)_3$	.05	*n*-Heptane	300	8	0	11.07[a]
$(C_5H_5)_2TiCl_2$-$Al(C_2H_5)_2$	.003	*n*-Heptane	40	8	7	0.4

[a] 66% of the product consists of hydrocarbons lower than decane.

Although the complex is a catalyst for the ethylene polymerization, less active than the catalyst prepared from $TiCl_4$ and $Al(C_2H_5)_3$, the composition of the complex strongly supports the hypothesis that the Ziegler type catalysts[8] for the polymerization of ethylene are, generally, bimetallic complexes containing organometallic bonds.

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(3) Decomposition of the complex by H_2SO_4 5%; titanium has been determined as titanium cupferrate, aluminum as 8-oxyquinolinate, chlorine by gravimetric determination (I. Ubaldini and F. Capizzi, *Chimica e Industria*, **37**, 779 (1955)).

(4 Decomposition of the complex by Na_2O_2; chlorine has been determined by the Volhard titration.

(5) By gas volumetric determination.

(6) By cryoscopic determination in benzene solution.

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ISTITUTO DI CHIMICA INDUSTRIALE
DEL POLITECNICO DI MILANO
MILANO, ITALY

GIULIO NATTA
PIERO PINO
GIORGIO MAZZANTI
UMBERTO GIANNINI

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A NOVEL REARRANGEMENT IN THE 5-NITRONORBORNENE SERIES

Sir:

The failure of salts of 5-nitronorbornenes (Ia, R = H[1]; Ib, R = CH_3[2]; Ic, R = C_6H_5[3,4]; shown in the aci form) to undergo the Nef reaction[5] has been attributed[6] to homoallylic[7] resonance stabilization (I ⟷ II) of the aci forms. We find, however, that, although a ketone is not obtained, Ia does yield a nitrogen-containing transformation product under Nef reaction conditions.

Addition of an ice-cold aqueous methanolic slurry of the sodium salt of Ia to 8.5% (by wt.) hydrochloric acid at −20 to −10° gave in 30–37% yields a rearrangement product (VI), m.p. 104.5–106.5°, isomeric with 5-nitronorbornene. *Anal.* Calcd. for $C_7H_9NO_2$ (139.15): C, 60.42; H, 6.52; N, 10.07. Found: C, 60.71; H, 6.63; N, 10.04; mol. wt. (Rast) 150. γ_{NH} 3380, 3150; $\gamma_{C=O}$ 1667; $\gamma_{C=C-H}$ 3040; $\gamma_{C=C}$ 1616 (shoulder) cm.$^{-1}$ in $CHCl_3$. As is true with hydroxamic esters,[8] VI and VII do not give a color test with ferric chloride and are weakly acidic; they can be extracted with ether from 10% sodium bicarbonate solution but not from 20% sodium hydroxide; they are regenerated upon acidification.

Hydrogenation of pure VI over platinic oxide at 2 atm. consumed 1.00 mole of hydrogen and gave in 96% yield a dihydro derivative (VII), m.p. 43–46°, $n^{25}D$ 1.5065 (on the supercooled liquid). *Anal.* Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.93. Found: C, 59.41; H, 7.79; N, 9.68. γ_{NH} 3180; $\gamma_{C=O}$ 1668 cm.$^{-1}$. Dichromate oxidation of VII and VIII gave glutaric acid.

Hydrogenation of VI over Raney nickel catalyst at 2 atm. (92% yield) or reduction of VII with iron powder and aqueous ethanolic ammonium chloride solution[9] yielded a tetrahydro derivative

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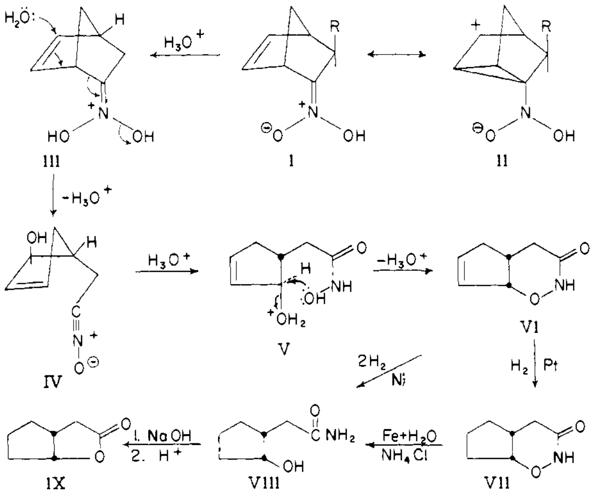
(VIII) of VI, m.p. 95.5–96°. *Anal.* Calcd. for $C_7H_{13}NO_2$ (143.18): C, 58.72; H, 9.15; N, 9.78. Found: C, 58.79; H, 8.98; N, 9.86; mol. wt. (Rast) 139; γ_{OH} 3500; γ_{NH} 3390, 1589; $\gamma_{C=O}$ 1668 in $CHCl_3$. VIII evolved a gas on treatment with nitrous acid. When warmed with 20% sodium hydroxide solution VIII evolved ammonia; under Schotten–Baumann conditions it yielded benzamide. Phenylurethan of VIII, m.p. 151.5–153.5°. *Anal.* Calcd. for $C_{14}H_{18}N_2O_3$: N, 10.68. Found: N, 10.67.



Warming VIII with 10–20% sodium hydroxide solution, followed by acidification, gave the known[10–13] lactone IX, b.p. 69° (0.5 mm.), $n^{25}D$ 1.4727, m.p. −13.5° to −12°. *Anal.* Calcd. for $C_7H_{10}O_2$ (126.15): C, 66.64; H, 7.99. Found: C, 66.54; H, 7.67; mol. wt. (Rast) 144; $\gamma_{C=O}$ 1759, 3520 (overtone; sample was shown to be pure by vapor phase chromatography). The infrared spectrum of our sample was identical with an authentic sample of IX,[11] and there was no depression in mixed m.p. Alkaline permanganate oxidation of our sample of IX gave glutaric acid; nitric acid oxidation of IX has been reported to give glutaric acid.[10]

The location of the double bond in VI has not been determined through chemical evidence; it is assigned tentatively on the basis of the mechanism (Ia → III → IV → V → VI) proposed to account for this novel fission of the norbornene ring system: Hydrolysis at C_2 of protonated Ia (III, or a more highly protonated version), with concerted shift of the double bond to C_3–C_4, fission of the C_4–C_5 bond, and elimination of hydroxyl to form the nitrile oxide IV. Hydrolysis of the nitrile oxide[14] to the hydroxamic acid followed by displacement, with inversion and ring closure, of the conjugate acid of the latter (possibly concerted as shown in V) would complete the *cis*-ring fusion of VI.

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SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA

WAYLAND E. NOLAND
JAMES H. COOLEY
PATRICIA A. MCVEIGH[15]

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SOLVENT EFFECTS IN THE REACTIONS OF FREE RADICALS AND ATOMS[1]

Sir:

Complexes between free radicals and aromatic hydrocarbons have been suggested,[2–5] but conclusive evidence supporting their existence is lacking. We have found that various aromatic solvents can drastically alter the position of attack of a chlorine atom on a branched-chain hydrocarbon and believe that this effect is connected with the ability of the aromatic hydrocarbon to form a complex with chlorine atoms. The data indicate that the complexed chlorine atom is much more selective than the free chlorine atom.

This effect was observed in the photochlorination of 2,3-dimethylbutane, analysis being performed by vapor phase chromatography. The 1- and 2-chloro-2,3-dimethylbutanes have retention times at 80° of 33 and 22 minutes, respectively, in a 2-m. B-column of a Perkin–Elmer model 154B Vapor Fractometer. Since we have previously demonstrated that the products of photochlorination are a true measure of the point of attack of the chlorine atom,[6] the relative reactivities of the tertiary and primary-hydrogen atoms were calculated by the equation

$$\text{Re. react. } (\textit{tert./prim.}) = \frac{\text{moles } \textit{tert.}\text{-chloride} \quad (12)}{\text{moles } \textit{prim.}\text{-chloride} \quad (2)}$$

TABLE I

PHOTOCHLORINATION OF 2,3-DIMETHYLBUTANE AT 55°

Solvent (4.0 molar)	Rel. react. (*tert./prim.*)
2,3-Dimethylbutane	3.7
Carbon tetrachloride	3.5
Methyl acetate	4.3
Nitromethane	3.4
Trichloroethylene	3.4
Propionitrile	4.0
Nitrobenzene	4.7
Benzoyl chloride	6.4
Benzotrifluoride	6.9
Chlorobenzene	10
Benzene	14
Benzene (25°)	20
o-Xylene	15
Mesitylene	17
t-Butylbenzene	24
1-Chloronaphthalene	37

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