duction of IV-semicarbazone in ethanol led to some ethyl ether. However, using potassium *tert*-butylate in *tert*-butyl alcohol, pure hydrocarbon II was obtained [liq., *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.7; H, 8.3. Found: C, 91.7; H, 8.5].

As a model, compound 1,2,3,6,7,8-hexahydro-*as*-indacene (V) was prepared from *o*-carboxymethylhydrocinnamic acid by successive ring-closure, hydrogenation, homologation to the propionic acid, ring-closure, and hydrogenation, using polyphosphoric acid for the cyclizations and palladium-on-carbon in the hydrogenations.

The chemical properties of II reflected a high degree of unsaturation. On standing, it absorbed oxygen and lost its ultraviolet absorption. Hydrogenation in methanol with palladized carbon proceeded very rapidly (20 min.) with the absorption of 300 mole % of hydrogen. At room temperature in chloroform, 300 mole % of perbenzoic acid was consumed and a diepoxyhydroxybenzoate was isolated. In comparative experiments, V was almost completely unreactive.

Comparison of the ultraviolet absorption of II with V, Fig. 1, shows a decreased extinction coefficient, a decided bathochromic shift (8 mμ), and the disappearance of fine structure. These effects must be attributed to ring-strain and departure from co-planarity.[2,3,4] Furthermore, the present case provides a clear-cut example of this effect since the absorbing systems of II and V are identically substituted. Thus we may conclude that sufficient strain has been produced in II to cause bending of the benzene ring and hence decreased resonance stabilization.

[2] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

[3] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

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PLATINUM HEXAFLUORIDE[1]

Sir:

Volatile hexafluorides have been reported for the adjacent group of elements W, Re, Os and Ir.[2,3] For platinum, the next and "noblest" member of this series, the highest fluoride that has been isolated is the tetrafluoride. In view of the improved techniques presently available for the preparation and handling of reactive fluorine compounds, an attempt was made to produce PtF_6. The reactor was constructed chiefly of Pyrex glass and contained the platinum in the form of a spiral filament Directly above and very close to the platinum filament was a surface cooled with liquid nitrogen. A reaction between the platinum and fluorine vapor at 300 mm. pressure was initiated by briefly passing a current through the platinum wire. The reaction continued exothermally as evidenced by the incandescence of the wire and stopped when either fluorine or platinum was consumed completely. The major product was a non-volatile yellowish brown solid (PtF_4) that uniformly coated the walls. In addition a volatile material collected on the liquid nitrogen cooled condenser. After purification this volatile fraction amounted to 1.4 g. compared to 10 g. of platinum wire reacted.

This volatile fraction has been identified as PtF_6 by vapor density determinations and chemical analysis. Approximate solid vapor pressures at 0° and 21° are 29 and 96 mm., respectively, in agreement with values extrapolated from the properties of the four adjacent hexafluorides.

Solid PtF_6, which melts at 56.7°, is dark red in color when viewed with a microscope although the massive material appears black. Its vapor is brownish red in color resembling bromine. Solid PtF_6 has been found to be isostructural with OsF_6 and IrF_6 by X-ray powder determinations.

Platinum hexafluoride is probably the least stable and most reactive of the known hexafluorides. When stored in Pyrex or quartz it decomposes slowly leaving a reddish brown residue. This may be due to photochemical decomposition or to a very slow reaction with glass. However, in nickel containers it may be stored for weeks at room temperature without any evidence of decomposition. A striking example of its reactivity occurred when 100 mg. of PtF_6 was stored in a container that previously had been used for storing NpF_6. After several days the PtF_6 was no longer present having been used up quantitatively in the formation of NpF_6 from some Np residue in the container. All subsequent studies with PtF_6 have therefore been made in new equipment in which more stable hexafluorides have not previously been handled.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. H. Simons, ed., "Fluorine Chemistry," Vol. I, Chap. 2, Academic Press, Inc., New York, N. Y., 1950.

[3] John G. Malm and Bernard Weinstock, "Osmium Hexafluoride and Its Probable Identity with the Previously Reported Octafluoride," paper presented at the 131st meeting of the American Chemical Society in Miami, April, 1957.

THE NITROSATION AND NITRATION OF AMINES AND ALCOHOLS WITH NITROGEN TETROXIDE

Sir:

We wish to report several new reactions of nitrogen tetroxide. These reactions (Table I) represent simple methods for the syntheses of nitrosamines, nitroamines, nitrites, and nitrates; they also illustrate that nitrogen tetroxide can react cleanly either as a nitrosating agent (path a) or as a nitrating agent (path b).

In each run of Table I, a 1 *M* solution of N_2O_4[1] in methylene chloride (distilled from P_2O_5) at the given temperature was added slowly to an excess of the organic reactant in the appropriate solvent at the same temperature. Precautions were taken to exclude oxygen, water and carbon dioxide. The reaction mixture was allowed to warm to room

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[1] A mixture of tank NO_2 (The Matheson Co.) and oxygen was passed over P_2O_5 and into a trap at −80°. The white crystals obtained were allowed to melt and the liquid N_2O_4 was removed as required with a calibrated pipet.

TABLE I

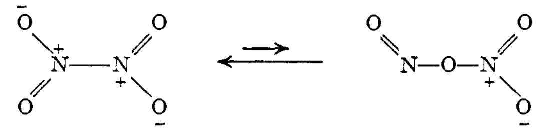
$$XH \text{ or } XNa + N_2O_4 \begin{cases} \xrightarrow{a} XNO + (H \text{ or } Na)NO_3 \\ \xrightarrow{b} XNO_2 + (H \text{ or } Na)NO_2 \end{cases}$$

Run	Reactant	Temp., °C.	Solvent	Yields,[a] % Path a		Path b	
1	$(C_2H_5)_2NH$	0	CH_2Cl_2	$(C_2H_5)NNO$ (98) [93],	$(C_2H_5)_2NH_2^+NO_3^-$ (95)	$(C_2H_5)_2NNO_2$ (0),	$(C_2H_5)_2NH_2^+NO_2^-$ (3)
2	$(C_2H_5)_2NH$	−80	CH_2Cl_2	(0)	(0)	(97) [93]	(100)
3	$(C_2H_5)_2NH$	−80	Ether	(39)	(40)	(59)	(59)
4	n-$C_4H_9O^-Na^+$	0	$CH_2Cl_2 + C_4H_9OH$	C_4H_9ONO (99)	$NaNO_3$ (97)	$C_4H_9ONO_2$ ..	$NaNO_2$ (1)
5	n-$C_4H_9O^-Na^+$	−80	$CH_2Cl_2 + C_4H_9OH$	(6)	(5)	(89)	(93)
6	n-$C_4H_9O^-Na^+$	−50	$CH_2Cl_2 + C_4H_9OH$	(51)	(52)	..	(48)
7	n-$C_4H_9O^-Na^+$	−80	CH_2Cl_2[b]	(26)	(37)	(56)	(56)
8	$C_6H_5CH_2CH_2OH$[c]	−80	CH_2Cl_2[b]	RONO (93)	HNO_3 (100)	$RONO_2$ (0)	HNO_2 (7)
9	n-$C_6H_{13}NH_2$	−80	CH_2Cl_2[b]	$C_6H_{13}OH$[d] ..	$C_6H_{13}NH_3^+NO_3^-$ (35)	$C_6H_{13}NHNO_2$ [53]	$C_6H_{13}NH_3^+NO_2$ (55)
10	$CH_3CON^-CH_3Na^+$	−80	CCl_4[b]	$CH_3CON(NO)CH_3$ (98)	$NaNO_3$ (100)	..	$NaNO_2^-$(0)

[a] Values in brackets refer to yields of isolated products. Values in parentheses were determined as follows: column 1, ultraviolet; column 2, see footnote 2; column 3, infrared; column 4, see footnote 3. [b] Heterogeneous runs (others homogeneous throughout run). [c] Allowed to stand for 24 hr. at −80° to complete the reaction. All others worked up as soon as reactants were mixed. [d] $C_6H_{13}ONO_2$ (6%) also was obtained.

temperature and the volatiles were removed under vacuum. Nitrate ion was determined in the residue by means of the nitron reagent[2] and nitrite ion was determined by the method of Stempel.[3] The organic products in the volatile fractions were determined spectrophotometrically (infrared and ultraviolet). Each organic product also was isolated and identified by a comparison of its properties and spectra with those of authentic samples.

The N_2O_4 reactions are unusually sensitive to conditions as illustrated by the effect of temperature (runs 1 and 2; 4, 5, and 6), the effect of base strength (runs 2 and 8, 8 and 5), the effect of solvent (runs 2 and 3), and the effect of heterogeneity (runs 5 and 7, 10). Previous to our work, it had been reported that ammonia,[4a] primary aromatic amines,[4b] and alcohols[4c] were nitrosated by N_2O_4. In no case was nitration observed.[5] Most of the chemical reactions of N_2O_4, therefore, involve nitrosation; nitration (as the primary reaction) occurs only at low temperatures, and then only with reactants that are strong bases. We interpret our results in terms of an equilibrium between I, the predominant form of nitrogen tetroxide,[6]



I II

and an isomeric form II.[7] The nucleophilic displacement of nitrite ion from I leads to nitration and the displacement of nitrate ion from II leads to nitrosation.[8]

We wish to thank the Research Corporation for its support of part of this work.

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[3] B. Stempel, *Z. anal. Chem.*, **91**, 413 (1933).

[4] (a) F. Falk and R. N. Pease, THIS JOURNAL, **76**, 4746 (1954); (b) B. Houston and T. B. Johnson, *ibid.*, **47**, 3011 (1925); (c) A. D. Yoffe and P. Gray, *J. Chem. Soc.*, 1412 (1951). For reaction with other organic compounds, see J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

[5] Riebsomer (footnote 4) has listed a number of cases where partial nitration was observed in other reactions of N_2O_4 (especially those at high temperatures where oxidation reactions occur).

[6] Structure I was assigned to crystalline N_2O_4 by J. S. Broadley and J. M. Robertson (*Nature*, **164**, 915 (1949)) and to gaseous N_2O_4 by O. W. Smith and K. Hedberg (*J. Chem. Phys.*, **25**, 1282 (1956)).

[7] The unsymmetrical form (II) has been invoked by a number of investigators to account for the nitrosations observed with N_2O_4, *e.g.*, F. Seel, *Z. anorg. Chem.*, **261**, 75 (1950).

[8] Similar reactions have been proposed by H. Taube and M. Anbar (THIS JOURNAL, **77**, 2993 (1955)) for the hydrolysis of N_2O_4.

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INITIATION OF STYRENE POLYMERIZATION AT A CATHODE

Sir:

Polymerization of styrene initiated by electrons has been observed when the monomer is exposed to the electric discharge of a Tesla coil,[1] β-irradiation,[2,3] and to cathode rays from a generator of the resonant transformer type.[4] Polymerization of styrene initiated by electrons supplied by the colored anion obtained by reaction of an aromatic hydrocarbon, such as naphthalene, with metallic sodium in a suitable solvent has also been noted.[5]

During the course of studies of reduction of organic compounds in anhydrous pyridine solution by unipositive magnesium anodically generated a novel and potentially valuable phenomenon was encountered, namely, the polymerization of styrene initiated by electrons supplied at a cathode. With styrene as additive, sodium iodide as electrolyte, and magnesium electrodes, electrolyses carried out at 30° for about 45 hr., in a divided cell[6] gave no

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[5] (a) N. D. Scott, U. S. Patent 2,181,771 (1939); (b) M. Szwarc, M. Levy and R. Milkovich, THIS JOURNAL, **78**, 2656 (1956); (c) M. Szwarc and A. Rembaum, *J. Polymer Sci.*, **22**, 189 (1956); (d) D. E. Paul, D. Lipkin and S. I. Weissman, THIS JOURNAL, **78**, 116 (1956).

[6] M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **76**, 3622 (1954).