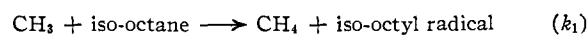


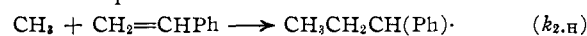
residual molecule is identical with that of the initial state.

To obtain further insight into the structure of this transition state, we compared the rates of addition of methyl radicals to hydrogen containing substrates with those observed in reactions involving deuterated analogs. If the configuration around the reactive center is changed considerably in the transition state, a variation in the rate constant of the respective addition reaction might be expected, and its magnitude then may be used to gauge the extent of deformation.

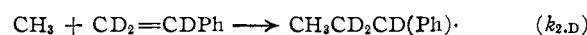
Using the approach developed by Streitwieser^{3,4} we calculate that a change of configuration at the reaction center from a trigonal to tetrahedral should lead to a ratio $k_D/k_H = 1.82$ for CH_3 addition to $\text{C}_6\text{H}_5\text{CD}=\text{CD}_2$ and $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ respectively at 50° . The actual data were obtained by determining the k_2/k_1 ratio for each of these compounds, where reaction (1) describes a hydrogen abstraction reaction



whereas reaction (2) describes the investigated addition process



or



The experimental technique and the methods of calculation of the results are described fully in a recent paper by Steel and Szwarc.⁵ All the pertinent data are given in Table I.

TABLE I

METHYL AFFINITIES OF STYRENE AND DEUTERIOSTYRENE
Solvent, iso-octane; T is 50° ; CH_3 radicals generated by photolysis of azo-methane; $\lambda \sim 3600 \text{ \AA}$.

Compound	Mole %	CH_4/N_2	k_2/k_1	
.....	0.0	0.560	..	
....	0.0	.554	..	
	Av.	0.557	..	
Styrene	.282	.130	1134	} Av. 1134
Styrene	.282	.130	1134	
Deuterostyrene	.189	.167	1214	} Av. 1214
Deuterostyrene	.189	.167	1214	
			$k_D/k_H = 1.07$	
....	.0	.582	..	
Styrene	.143	.229	1076	} Av. 1084
Styrene	.143	.227	1091	
Deuterostyrene	.142	.214	1208	} Av. 1208
Deuterostyrene	.142	.214	1208	
			$k_D/k_H = 1.11$	

The results listed in Table I show clearly that, as has been expected, the deuteration accelerates the rate of methyl radical addition. The magnitude of the observed effect (7–11%) is much lower than that calculated on the assumption of the tetrahedral transition state (82%). We conclude, therefore, that these results indicate only a slight deviation of the transition state configuration from

(3) A. Streitwieser and R. C. Fahey, *Chem. and Industry*, 1417 (1957).

(4) A. Streitwieser, R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(5) C. Steel and M. Szwarc, *J. Chem. Phys.*, **33**, 1677 (1960).

that of the initial state. Hence, we confirm the tentative assumption made in previous papers from this laboratory.²

The smallness of the effect observed here suggests also that the incipient C–CH₃ bond, formed in the transition state, is comparatively long. Furthermore, it is clear that the concept of addition close to the nodal plane, which was advocated in our previous paper,⁶ is definitely erroneous.

In conclusion we give thanks to Dr. Leo Wall for the gift of deuterated styrene, to Dr. A. Streitwieser for his helpful discussions, and to the National Science Foundation for a grant.

(6) A. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 5621 (1957).

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A NOVEL REARRANGEMENT OF PYRIMIDINES TO *s*-TRIAZINES¹

Sir:

5-Nitroso-6-aminopyrimidines are widely employed intermediates for the synthesis of purines, pteridines and other condensed pyrimidine heterocycles and are prepared readily by a variety of synthetic methods.^{2,3} We wish to report a novel rearrangement of these intermediates to 2-cyano-*s*-triazines.

Heating a mixture of 2-phenyl-4,6-diamino-5-nitrosopyrimidine (I, R = Ph, X = NH) for one hour with 1.1 equivalents of benzenesulfonyl chloride and excess pyridine, or with 1.1 equivalents of phosphorus oxychloride and excess pyridine, or simply with excess thionyl chloride, gave 2-cyano-4-phenyl-6-amino-*s*-triazine, m.p. 207° (V, R = Ph, X = NH)⁴ in 30% yield. The structure of this compound was confirmed by sulfuric acid hydrolysis to 2-carboxamido-4-phenyl-6-amino-*s*-triazine, m.p. 324° , then treatment with potassium hypochlorite to give benzoguanamine (2-phenyl-4,6-diamino-*s*-triazine), identical with an authentic sample.⁵ Similarly, heating 2-dimethylamino-4-hydroxy-5-nitroso-6-aminopyrimidine (I, R = N(CH₃)₂, X = O) and 2-methylthio-4,6-diamino-5-nitrosopyrimidine (I, R = SCH₃, X = NH) for 5–30 minutes with excess acetic anhydride gave 2-cyano-4-dimethylamino-6-hydroxy-*s*-triazine, m.p. 262° (V, R = N(CH₃)₂, X = O), 84% yield, and 2-cyano-4-methylthio-6-acetylamino-*s*-triazine, m.p. 213° (V, R = SCH₃, X = NCOCH₃), 100% yield, respectively. 2,4-Diamino-5-nitroso-6-hydroxypyrimidine (I, R = NH₂, X = O) rearranged to 2-cyano-4-amino-6-hydroxy-*s*-triazine,

(1) This work was supported in part by a grant (C-2551) to Princeton University from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) B. C. Taylor, O. Vogl and C. C. Cheng, *J. Am. Chem. Soc.*, **81**, 2442 (1959).

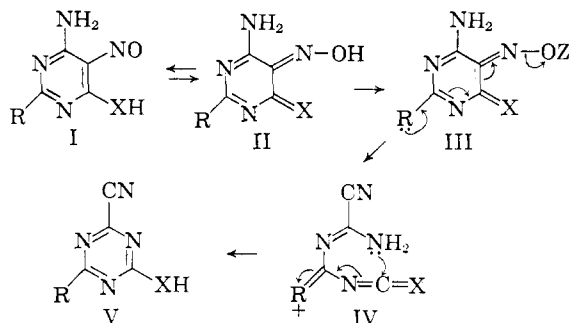
(3) A. Bendich in "The Nucleic Acids, Chemistry and Biology," ed. by E. Chargaff and J. N. Davidson, Vol. I, Academic Press, Inc., New York, N. Y., 1955, p. 81.

(4) Acceptable microanalytical results were obtained for all compounds reported.

(5) We are indebted to the American Cyanamid Company for a generous gift of authentic material.

m.p. $> 350^\circ$ (V, R = NH₂, X = O) upon heating for a few minutes with trifluoroacetic anhydride.

We believe that these transformations are initiated by esterification of the 5-nitrosopyrimidine in its oxime form (II) to give III (Z = SO₂C₆H₅, COCH₃, COCF₃). Elimination of ZO⁻ with cleavage of the C₄-C₅ bond then yields the open-chain intermediate IV in a reaction closely related to the "fragmentations" discussed by Grob.⁶ Recyclization gives the observed products (V). This interpretation is consistent with the observation that the transformation is facilitated markedly by the introduction of electron-releasing substituents (e.g., N(CH₃)₂, SCH₃) in the 2-position of the pyrimidine ring.



The reaction appears to be general for 5-nitroso-6-aminopyrimidines and represents a convenient method for the preparation of cyano-*s*-triazines.

(6) C. A. Grob in "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publications, London, 1959, p. 114.

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COMPLEX CARBONYL HYDRIDES OF OSMIUM AND RUTHENIUM

Sir:

We have reported recently the discovery and some properties of monohalogeno complexes of osmium and ruthenium with triphenylphosphine and triphenylarsine which were obtained from the simple system of metal salt [(NH₄)₂OsX₆, RuX₃], ligand and alcohol (2-methoxyethanol or ethylene glycol, 120–190°).^{1,2} Based on analytical and conductivity data, these compounds were formulated as containing univalent metal, [MXL₃] (M = Os, Ru; X = Cl, Br; L = Ph₃P, Ph₃As). Thus, in the absence of a direct evidence to the contrary, decomposition of solvent alcohol and coordination of its fragments to the metal were not considered, following the theretofore accepted assumption in the preparative coordination chemistry. Since then, however, it has been demonstrated that metal-hydrido complexes may be formed readily by reaction with alcohol in similar systems.³ And Chatt and Shaw⁴ have reported to have obtained also carbonyl complexes from a related environment (ethanol + KOH), citing as evidence

(1) I. Vaska, *Z. Naturforschg.*, **15b**, 56 (1960).

(2) L. Vaska and E. M. Sloane, *J. Am. Chem. Soc.*, **82**, 1263 (1960).

(3) L. Vaska, *ibid.*, **83**, in press (1961).

(4) J. Chatt and B. L. Shaw, *Chem. and Ind.*, 931 (1960).

strong bands near 1900 cm.⁻¹ in the infrared spectrum which are attributed to $\gamma_{C=O}$. In view of these observations, and particularly since we have found similar strong absorptions at 1800–2100 cm.⁻¹ in the spectra of a number of mono-, di- and trihalogeno complexes of osmium and ruthenium, some of which, as we now find, are formed even at 25° (including monohalides),⁵ we have undertaken a study of these reactions by using radiocarbon and deuterated alcohols as solvents.

According to the evidence obtained from these experiments, summarized below, we now wish to reformulate the monohalogeno complexes of Os and Ru as containing also hydrido and carbonyl groups, [MHX(CO)L₃] (cf. ref. 4).

TABLE I

Compound	Infrared spectrum (cm. ⁻¹) ^a			Oxygen, %		No. of ¹⁴ C/ f.w. of compd.
	ν_{M-H}	ν_{M-D}	$\nu_{C=O}$	Found	Calcd.	
[RuHCl(CO) (Ph ₃ P) ₃]	2020	1457	1916	1.8	1.7	1.02
[OsHCl(CO) (Ph ₃ P) ₃]	2100	1505	1898	1.6	1.5	1.05
[OsHBr(CO) (Ph ₃ P) ₃]	2105	1509	1902	1.4	1.3	0.85

^a ± 5 cm.⁻¹; halocarbon mull. ^b $\nu_{M-H}/\nu_{M-D} = 1.39$ to 1.40; calcd., 1.41.

The presence of a metal-hydrogen bond and the assignment of ν_{M-H} are indicated by the isotopic shift in the infrared spectrum. The metal deuterides (or hydride-deuteride mixtures) were prepared by either refluxing a suspension of the complex in C₂H₅OD, or directly from the metal salt, Ph₃P and deuterium-enriched 2-methoxyethanol (120°) or ethylene glycol (180°).

The unusual reaction of Os and Ru halides with alcohols leading to carbonyl complexes was studied by synthesizing the compounds in the usual manner except using ¹⁴C-ethylene glycol as solvent (190°). The products, after being washed extensively (methanol) and dried (vacuum), were dissolved in toluene scintillator solution and the activity counted. The absolute activity of the samples was compared with that of the starting ¹⁴C-ethylene glycol by adding standard ¹⁴C-toluene to the samples.

The results (Table I) indicate that one carbon atom of the ethylene glycol is incorporated per formula weight of the complex. The analytical data do not, except for oxygen, readily distinguish between the previous and present formulation of these complexes. Repeated oxygen analyses have now established that M/O = 1. According to the infrared spectra this oxygen is not associated with either —OH or triphenylphosphine oxide (possible forms of oxygen that have been observed to be present in other compounds obtained from the same systems), which, altogether, appears to confirm the suggested composition and the assignment of $\gamma_{C=O}$.

The authors are indebted to Dr. R. H. Schuler of the Radiation Research Laboratories of this Institute for valuable suggestions and help in carrying out counting experiments, for supplying radiocarbon alcohols and making equipment available in his laboratories. They also wish to thank