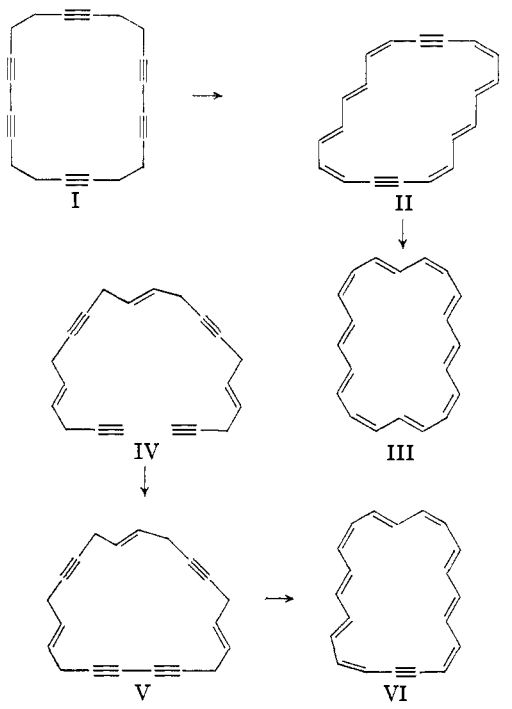

plates from pentane (red-brown in solution), m.p. 176–177° dec.[4]; $\lambda_{max}^{isooctane}$ 319 and 336 mμ (ε 109,000 and 74,000); acetylene band at 4.64 μ in the infrared (KBr). Full hydrogenation again led smoothly to cycloeicosane, m.p. and mixed m.p. 59–60°. The isomerization product is clearly a fully conjugated cycloeicosaoctaene-diyne and a symmetrical 1,11-diyne structure (II or a stereoisomer) appears most probable. The substance was reasonably stable and could be kept without appreciable change in light and air at room temperature for 24 hr in the solid state or for 12 days in dilute benzene solution.

Partial hydrogenation of II in benzene over a "Lindlar" palladium catalyst and then careful chromatography on alumina yielded first a yellow oily substance and then unchanged starting material. The yellow product appears to be cycloeicosadecaene (III or a stereoisomer) in view of the ultraviolet spectrum [$\lambda_{max}^{isooctane}$ 267, 284, 297, 375 and 396 mμ (ε 0.81, 0.83, 0.81, 0.20 and 0.19)],[5] the infrared spectrum (absence of acetylene band in the 4.5–4.7 μ region) and full hydrogenation to cycloeicosane, m.p. 55–58°. Further structural evidence is provided by the fact that potassium *t*-butoxide rearrangement of *trans-trans*-1,11-cycloeicosadiene-5,7,15,17-tetrayne (I, replace single acetylenes by *trans*-double bonds), a reaction which also was expected to yield III or a stereoisomer, had led to crude yellow oily chromatography fractions with similar ultraviolet properties [*e.g.* $\lambda_{max}^{pentane}$ 268–272, 283, 297, 312, 373 and 394 mμ (ε 1.13, 1.61, 0.87, 0.69, 0.26 and 0.24)].[1]

The nonaene-yne VI was prepared: *trans*-1,4-dibromo-2-butene on reaction with an excess of ethynylmagnesium bromide in tetrahydrofuran in the presence of cuprous chloride furnished besides other products[6] *ca.* 3% of all-*trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (IV) (m.p. 99–100°; no high-intensity absorption in the ultraviolet; found: C, 91.89; H, 7.69; converted by full hydrogenation to *n*-eicosane, m.p. and mixed m.p 36–37°). Oxidation with cupric acetate in pyridine[3] at 70° for 5 hr. yielded 18% of the colorless cyclic monomer, all-*trans*-1,7,13-cycloeicosatriene-4,10,16,18-tetrayne (V) [m.p. 116–117°; $\lambda_{max.}^{ether}$ 229, 238 and 254 mμ (ε 480, 470 and 240); found: C, 92.60; H, 6.75], which on full hydrogenation gave cycloeicosane, m.p. and mixed m.p. 61–62°.

Compound V was rearranged with potassium *t*-butoxide in *t*-butyl alcohol–benzene at *ca.* 55° for 90 seconds. The least polar fractions obtained after chromatography on alumina gave *ca.* 20% of a compound which appears to be cycloeicosanonaenyne (VI or a stereoisomer). It was obtained as a yellow oil [λ_{max}^{ether} 260, 270, 281 (infl.) and 340 mμ (ε 48,000, 47,000, 41,000 and 15,700)[5]; acetylene band at 4.53 μ in the infrared (chloroform)], which on full hydrogenation once more gave cycloeicosane (m.p. 56–58°). In addition a substance was isolated in *ca.* 2% yield from the most polar chromatography fractions which is most probably another isomer of VI. This isomer formed dark red crystals [red-brown in solution; λ_{max}^{ether} 281 and 322 mμ (ε 0.45 and 0.54)] but it was obtained in too small quantity for further study. Both the isomers of VI as well as the decaene III were unstable and soon decomposed on standing either neat or in solution.

(5) That all the ultraviolet maxima belong to the same chromophore was shown by the fact that all the chromatography fractions containing this substance showed essentially identical spectra and remained unchanged on re-chromatography,

(6) See F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765, (1960).

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SECONDARY DEUTERIUM EFFECT IN METHYL RADICALS ADDITION REACTION. STRUCTURE OF THE TRANSITION STATE[1]

Sir:

Addition of methyl radicals to olefinic, acetylenic or aromatic compounds leads to formation of new C–C bonds. The reactive center in each class of these compounds involves a carbon atom, although a different configuration characterizes each group. For example, in olefins the center (C*) is in a $C{=}C^{*}{<}^{H}_{H}$ moiety, whereas in aromatic hydrocarbons the structure is $\overset{C}{C}{>}C^{*}{-}H$. In previous communications from this laboratory[2] it was suggested that in radical addition reactions the initial structure of a reactive center is preserved in the transition state. The best argument in favor of this suggestion is found in the excellent linear relation between logs of the relevant rate constants per reactive center and the corresponding localization energies, since the latter were calculated on the assumption that the nuclear framework of the

(1) This work was supported by the National Science Foundation.

(2) (a) M. Szwarc aud J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, Butterworth Publications, London, 1959, p. 262; (b) J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).

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 $C_6H_5CD{=}CD_2$ and $C_6H_5CH{=}CH_2$ 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

$$CH_3 + \text{iso-octane} \longrightarrow CH_4 + \text{iso-octyl radical} \qquad (k_1)$$

whereas reaction (2) describes the investigated addition process

$$CH_3 + CH_2{=}CHPh \longrightarrow CH_3CH_2CH(Ph)\cdot \qquad (k_{2,H})$$

or

$$CH_3 + CD_2{=}CDPh \longrightarrow CH_3CD_2CD(Ph)\cdot \qquad (k_{2,D})$$

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; $\lambda \sim 3600$ Å.

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 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–CH_3 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.

(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).

(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*-TRIAZINES[1]

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 = $N(CH_3)_2$, X = O) and 2-methylthio-4,6-diamino-5-nitrosopyrimidine (I, R = SCH_3, X = NH) for 5–30 minutes with excess acetic anhydride gave 2-cyano-4-dimethylamino-6-hydroxy-*s*-triazine, m.p. 262° (V, R = $N(CH_3)_2$, X = O), 84% yield, and 2-cyano-4-methylthio-6-acetylamino-*s*-triazine, m.p. 213° (V, R = SCH_3, X = $NCOCH_3$), 100% yield, respectively. 2,4-Diamino-5-nitroso-6-hydroxypyrimidine (I, R = NH_2, 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) E. 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.