could be prepared from cholesterol acetate in two steps. The only uncertainty at this stage would be the effect of the chlorine atom at position 5 on the microorganism. However, the presumed intermediate, β-chloro ketone, should eliminate HCl easily even in the fermentation medium. When 1.1 g. of V was exposed to CSD-10 for 80 hr., 250 mg. (36%) of I, m.p. 179–182°, was obtained.

Surprisingly, 3-hydroxycholesta-1,3,5(10)-triene (VI) was not metabolized by CSD-10.[13]
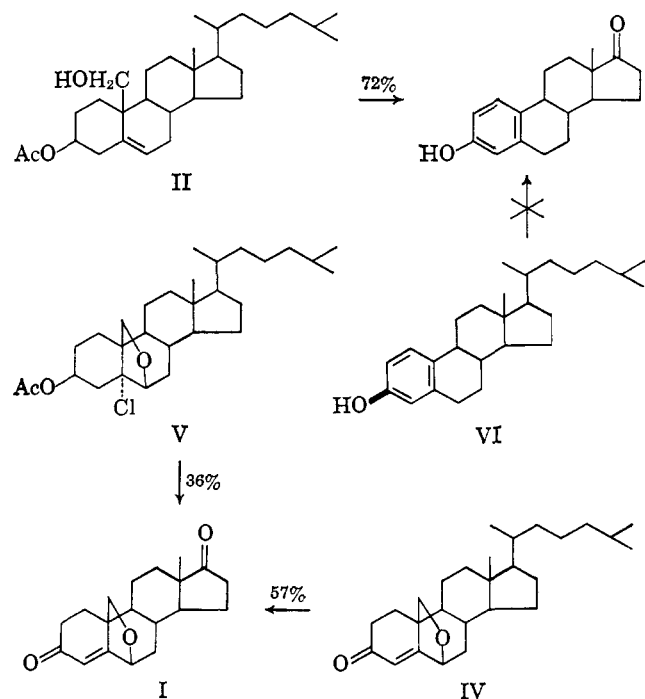
It is our contention that the major pathway of cholesterol degradation by this microorganism must first involve the removal of the side chain to yield a C-19 steroid which is then metabolized *via* the 9,10-seco pathway of Dodson and Muir.[14] By blocking the introduction of the 1,2-double bond through the formation of a 6,19-oxido bridge or by interfering with the 9α-hydroxylation process through the introduction of a hydroxyl function at C-19,[15] the desired intermediate, I, and estrone accumulated. Table I shows that androst-4-ene-3,17-dione is an effective inducer and substrate for both the 9α-hydroxylase and 1-dehydrogenase. On the other hand, cholest-4-en-3-one apparently is an extremely poor inducer of both of these enzymes and could not act as a substrate for the 9α-hydroxylase. But it is a substrate for the 1-dehydrogenase. This is consistent with the fact that we have been unable to detect the presence of 9α-hydroxylated products in the C-27 series whereas a small quantity of VI was detected when 19-hydroxycholest-4-en-3-one was used as the substrate.

The results herein presented describe a four-step synthesis of estrone and a three-step synthesis of I from cholesterol acetate. To our knowledge, this probably

(13) It is interesting to note that Turfitt reported [*Biochem. J.*, **42**, 376 (1948)] that many *Proactinomyces* strains, after prolonged culture upon estradiol as sole carbon source, showed a diminution in their capacity for oxidizing cholesterol.
(14) R. M. Dodson and R. D. Muir, *J. Am. Chem. Soc.*, **83**, 4627 (1961).
(15) 19-Hydroxyandrost-4-ene-3,17-dione is considerably less efficient as an inducer and substrate for the 9α-hydroxylase than androst-4-ene-3,17-dione.

constitutes the most economical processes to date for the preparation of estrone and 19-norsteroids.[16]

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Electron and Energy Transfer in Irradiated Xenon–Hexane Liquid Solutions

Sir:

We have measured the dimer and hexene yields in Co^{60} γ-irradiated xenon–hexane liquid solutions at −78° and compared them with those for pure hexane.[1] Both dimers and hexenes are formed in yields corresponding to essentially complete electron energy transfer even at 0.04 mole fraction of hexane in xenon. Furthermore, the distribution of the six dimers and five hexenes is similar for all mole fractions studied. Thus we can conclude that the precursors of the observed products must be substantially the same whether they arise from energy transfer or direct radiolysis. We postulate that electron transfer from hexane to ionized xenon is the predominant mechanism of energy transfer (which process is exothermic, 1.7 e.v. in the gas phase[2]), and that the product precursors are hexane ions, although this can hardly be said to have been established beyond question. We believe our results demonstrate in a simple way a very efficient energy transfer in a novel liquid system. Previously, Bouldin and Gordy[3] demonstrated energy transfer in krypton matrices at 4.2°K. containing 10^{-4} and 10^{-1} mole fraction of methane by e.s.r. observation of trapped hydrogen atoms, and Borkowski and Ausloos[4] studied the effects of adding noble gases on the radiolysis of gaseous isobutane. Electron transfer is much more easily studied in gas mixtures by mass spectrometry, and the rate constants so determined are among the fastest known in all of reaction kinetics.[5,6] Electron transfer can occur rapidly over distances of several atomic diameters even when tunneling is required.[6]

(1) (a) L. Kevan and W. F. Libby, *J. Chem. Phys.*, **39**, 1288 (1963); (b) H. Widmer and T. Gaumann, *Helv. Chim. Acta*, **46**, 944 (1963); (c) *ibid.*, **46**, 2780 (1963).
(2) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.
(3) W. V. Bouldin and W. Gordy, *Phys. Rev.*, **135**, A806 (1964).
(4) R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, **38**, 36 (1963).
(5) F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, London, 1961, p. 69.
(6) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

	Hexane mole fraction			
	1.0	0.10	0.076	0.043
	G values, molecules per 100 e.v. absorbed			
$4,5\text{-}Et_2C_8$	0.13	0.09	0.13	0.11
$4\text{-}Et\text{-}5\text{-}MeC_9$	0.25	0.21	0.22	0.31
$5,6\text{-}Me_2C_{10}$	0.12	0.11	0.14	0.12
$5\text{-}MeC_{11} + 4\text{-}EtC_{10}$	0.30	0.47	0.32	0.71
$N\text{-}C_{12}$	0.06	0.04	0.05	0.04
Total dimer	0.86	0.92	0.85	1.3
trans-2-Hexene	0.90	0.9	0.75	1.0
1-Hexene	0.45	~0.2	0.30	0.12
cis-2-Hexene	0.20	~0.04	0.3	~0.02
trans-3-Hexene	0.10	~0.2	0.5	~0.2
cis-3-Hexene	~0.05	~0.2	0.25	~0.1
Total hexenes	1.7	~1.5	2.1	1.4

Liquid solutions of xenon and hexane were made by preparing a gas phase mixture in a vacuum line, freezing it into a 13-mm. Pyrex tube with a break seal and 2-mm. thick walls, and sealing at 77°K. By warming to −78°, corresponding to a xenon vapor pressure of 4 atm., the liquids were clearly observed to be miscible in all proportions. These liquid solutions were thoroughly mixed and irradiated by Co^{60} at −78° to a dose varying from 0.3 to 1.5 Mrads (1 Mrad = 10^8 erg/g.) for samples with hexane mole fraction ranging from 0.04 to 1. After irradiation the samples were refrozen, opened to high vacuum, and slowly warmed to about −80° (hexane m.p. −94°) while the xenon was collected in a bulb; the liquid hexane was warmed to about 0° and removed for analysis by v.p.c.[1] Doses absorbed by the solutions were calculated using theoretical "mass energy absorption coefficients"[7] of 0.0301 cm.²/g. for the dosimeter (0.1 N H_2SO_4), 0.315 cm.²/g. for hexane, and 0.0251 cm.²/g. for xenon; these coefficients take into account a photoelectric energy absorption of 11% in xenon.

The dimer and hexene yields are presented in Table I. They show that all eleven products result from a very efficient energy-transfer mechanism in the liquid solutions. The simplest interpretation of these results is that electron transfer from hexane to xenon ions produces hexane ions and possibly excited molecules and free radicals that are quite comparable to the entities responsible for product formation in the radiolysis of pure hexane.[1] Establishment of transfer of pure subionization excitation is difficult due to lack of knowledge concerning the excited states of hexane. An isolated xenon atom has its lowest metastable excited state at 8.32 e.v.,[8] while in solid xenon at 4.2°K. the value is 8.24 e.v.[8] The lowest state for hexane probably lies in this range[9] also, so excitation transfer may or may not be exothermic. If excitation transfer were the primary mode, one would expect on the basis of McNesby's results[10] that H_2 ejection to form hexenes would be the dominant process and that the proportion of dimers would decrease in the solutions of low hexane mole fraction. These expectations are clearly

(7) National Bureau of Standards Handbook, Vol. 84, U. S. Government Printing Office, Washington, D. C., 1962, p. 7.

(8) O. Schnepp and K. Dressler, ibid., 33, 49 (1960).

(9) E. N. Lassettre and S. A. Francis, J. Chem. Phys., 40, 1208 (1964).

(10) C. L. Currie, H. Okabe, and J. R. McNesby, J. Phys. Chem., 67, 1494 (1963), and earlier papers cited therein.

not attained and the results again favor electron transfer.

We therefore interpret these results in favor of our previous postulates[1a] of the importance of ionized states in the radiation chemistry of hexane. Growing support for these ideas is found in observations that substantial yields of "free" or trapped electrons have appreciable lifetimes in irradiated solid[11] and liquid hydrocarbons.[12]

(11) (a) J. P. Guarino and W. H. Hamill, J. Am. Chem. Soc., 86, 777 (1964); (b) M. Burton, M. Dillon, and R. Rein, J. Chem. Phys., 41, 2228 (1964).

(12) G. R. Freeman, ibid., 39, 988 (1963).

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Platinum Metal Sulfides as Heterogeneous Hydrogenation Catalysts

Sir:

Platinum metal sulfides,[1,2] i.e., the sulfides of ruthenium, rhodium, palladium, osmium, iridium, and platinum, have been found to be an important, hitherto unexploited class of heterogeneous hydrogenation catalysts.[3] In general, they behave like the base metal sulfide catalysts[4,5] but usually are considerably more active and more stable under hydrogenation conditions. They have been used effectively as bulk or supported catalysts, either preformed or prepared in situ, and in both liquid phase and vapor phase hydrogenations.

Each of the platinum metal sulfides was shown capable of catalyzing the hydrogenation of nitrobenzene to aniline.[3] These catalysts are considerably less active for this reaction than the commonly used and very efficient palladium catalyst. There are, however, at least two situations in which the platinum metal sulfides have particular utility for reductive aminations.

The first takes advantage of their insensitivity to poisons. For example, bis(4-nitrophenyl) sulfide was readily hydrogenated to bis(4-aminophenyl) sulfide with a rhodium sulfide catalyst.[3] This example illustrates, in addition to the lack of sulfur poisoning, the selective activity of the catalyst for reduction of a nitro group without hydrogenolysis of the thioether linkage.

A second important application is in the reduction of halogen-containing nitro compounds to amines without dehalogenation. Several halo-substituted nitrobenzenes were investigated. There was no detectable

(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, pp. 1461–1614.

(2) "Encyclopedia of Chemical Technology," Vol. 10, R. E. Kirk and D. Othmer, Ed., Interscience Encyclopedia Inc., New York, N. Y., 1953, pp. 838–854.

(3) U. S. Rubber Co., Belgian Patent 643,911 (March 13, 1964).

(4) H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis, J. Am. Chem. Soc., 76, 1519 (1954), and references therein.

(5) F. S. Dovell and H. Greenfield, J. Org. Chem., 29, 1265 (1964).