Table I. Dimer and Hexene Yields Based on Total Energy Absorbed by Solution

	Hexane mole fraction			
	1.0	0.10	0.076	0.043
	G values, molecules per 100 e.v. absorbed			
4,5-Et$_2$C$_8$	0.13	0.09	0.13	0.11
4-Et-5-MeC$_9$	0.25	0.21	0.22	0.31
5,6-Me$_2$C$_{10}$	0.12	0.11	0.14	0.12
5-MeC$_{11}$ + 4-EtC$_{10}$	0.30	0.47	0.32	0.71
N-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$_2$SO$_4$), 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).

dechlorination with the sulfides of palladium, platinum, rhodium, and ruthenium; no detectable debromination with platinum sulfide, trace debromination with rhodium sulfide, and appreciable debromination with palladium sulfide.

The selective hydrogenation of haloaryl nitro compounds also is applicable to polyhalo-substituted aromatics. For example, 2,5-dichloronitrobenzene was quantitatively hydrogenated to 2,5-dichloroaniline without dehalogenation when using a platinum sulfide catalyst.

Results of a large number of preparative experiments[3,6] plus development studies[6] have clearly demonstrated the superiority of platinum metal sulfide catalysts for the reductive alkylation of primary arylamines, or their nitro precursors, with aliphatic ketones. They usually produce a pure product with little or no side reactions, require no excess above the stoichiometric amount of ketone, and are active at relatively low pressures of hydrogen.

Platinum metal sulfide catalysts may be used for the reductive alkylation of aliphatic amines and their nitroalkane precursors with aliphatic ketones.[3] These catalysts might be of value when the feed contains a poison that prevents the use of other catalysts.

The platinum metal sulfides are useful for the selective hydrogenation of aryl disulfides to the corresponding thiophenols, e.g., phenyl disulfide to thiophenol, without further reduction to the hydrocarbon and hydrogen sulfide.[3] Cleavage of the thioether linkage, as in phenyl sulfide, requires very severe conditions under which the thiophenol formed is further reduced to the hydrocarbon.[3] On the other hand, this lack of reactivity for carbon–sulfur bond cleavage permits the selective reduction of other functional groups in thioethers, e.g., the previously mentioned conversion of a bis(nitrophenyl) sulfide to the corresponding bis(aminophenyl) sulfide.

Phenyl sulfone was very resistant to hydrogenation with a rhodium sulfide catalyst, there being no detectable reaction at 290° and over 122 atm.[3] There was little or no hydrogenation of arylsulfonic acids, arylsulfonic acid salts, or arylsulfonamides with a platinum sulfide catalyst at 240–250° and pressures of 95–122 atm.

The relative inactivity of these catalysts for the hydrogenation of aromatic rings, ketones, nitriles, esters, and some other functional groups, sometimes under severe reaction conditions, often permits useful selectivity in the hydrogenation of polyfunctional compounds. It also allows a wide choice of solvents for the hydrogenation reactions.

A typical reductive amination experiment follows. To a 600-ml. stainless-steel Magne-Dash autoclave were added 103.5 g. (0.54 mole) of 2,5-dichloronitrobenzene (Eastman Kodak 187), 230 ml. of methanol, and 3.0 g. of 5% platinum sulfide on carbon.[7] The autoclave was sealed and purged first with nitrogen and then with hydrogen. Hydrogen was added to a pressure of 41 atm. and the reaction mixture then was heated for 1.25 hr. at 85° and 34–54 atm., at which point gas absorption stopped at approximately the theoretical usage of hydrogen. The autoclave was

cooled and vented, and its content filtered to remove the catalyst. The filtrate was made strongly alkaline with dilute sodium hydroxide and the methanol solution was concentrated by distillation. Benzene was added and the remaining methanol was removed by distillation. The benzene solution then was cooled and washed with water. The combined aqueous solutions gave a negative test for chloride anion with silver nitrate; thus there had been negligible dehalogenation. The benzene solution was distilled up to a pot temperature of 207° at atmospheric pressure. The residue consisted of 87 g. (99.5% yield) of 2,5-dichloroaniline that melted at 48–49.5°; there was no depression on a mixture melting point with an authentic sample.

A typical reductive alkylation experiment is here described. To a 600-ml. stainless-steel Magne-Dash autoclave were added 158 g (0.86 mole) of N-phenyl-p-phenylenediamine, 95.2 g. (0.95 mole) of methyl isobutyl ketone, and 3.2 g. of 5% platinum sulfide on carbon.[7] The autoclave was sealed and purged with nitrogen and then with hydrogen, and hydrogen was added to a pressure of 27 atm. The autoclave was heated for 4.5 hr. at 175–180° and 27–41 atm. The vessel was cooled and vented, and the reaction mixture was removed. The catalyst was removed by filtration. After topping the filtrate to a pot temperature of 188° at 32 mm. there was obtained 228 g. (99% yield) of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine as a residue product melting at 45–47°.

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Marasmic Acid

Sir:

The evidence presented here requires that the terpenoid antibiotic, marasmic acid, have the nonisoprenoid structure 1. The natural occurrence of such a molecule provides circumstantial evidence for the existence of an interesting biosynthetic pathway in farnesyl ester cyclization from which other modified sesquiterpenoids are accessible.

Marasmic acid,[1] m.p. 173–174°, $[\alpha]_D$ +182°, has the empirical formula $C_{15}H_{18}O_4$.[2] One oxygen atom is present in an α,β-unsaturated aldehyde [λ_{max} 241 mμ (ϵ 9700); ν_{max} 1684 and 1631 cm.$^{-1}$; singlet, τ 0.53, 1 H] with a β-vinylic proton (doublet, $\tau \sim 3.50$, $J \sim 2$ c.p.s.). The remaining three oxygen atoms are contained in a γ-lactol (ν_{max} 3350 and 1773 cm.$^{-1}$) in which there is a proton attached to the lactol ether terminus (singlet, τ 3.87, 1 H). On methylation (diazomethane) marasmic acid is converted into the methyl ester 2 (ν_{max} 1724 cm.$^{-1}$) of a dialdehydecarboxylic acid (doublet, τ 3.45, 1 H, $J \sim 2$ c.p.s.; singlet, τ 0.52,

(6) F. S. Dovell and H. Greenfield, unpublished work.
(7) Commercially available from Engelhard Industries, Inc.

(1) F. Kavanagh, A. Hervey, and W. J. Robbins, Proc. Natl. Acad. Sci. U. S., 35, 343 (1949).
(2) Adequate analyses have been recorded for all substances reported. Where not specifically mentioned all spectroscopic data are in agreement with the assigned structures.