decafluoro-4-methyl-4-heptanol (IV), b.p. 132–133°, n^{20}_D 1.3031, d^{25} 1.763, was obtained, along with a 67% yield of hexafluoropropene. The recovery of III was 36%. An infrared spectrum of IV agreed with the structure proposed.[31]

Procedure C.—Solid methyllithium was added to a mixture of the ketone and an excess of the iodide in the absence of ether. The exchange reaction proceeded normally to form heptafluoropropyllithium. Evidence for this was a 65–70% yield of hexafluoropropene. No other product was isolated, and 53% of the ketone was recovered.

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[31] Haszeldine[7] has reported this alcohol from reactions of heptafluoropropylmagnesium iodide with acetyl chloride or ethyl acetate. No properties or other data were given.

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Specificity of Nickel Catalysts. Effect of Dimethyl Disulfide upon Hydrogenation of Olefinic Hydrocarbons

BY HERMAN PINES, JOSEPH MARECHAL[1] AND W. S. POSTL

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It was reported previously[2] that the presence of small amounts of sulfur-containing compounds can greatly influence the type of activity of a nickel catalyst. Thus in the absence of sulfur compounds primary alcohols are dehydroxymethylated at 250° and under 100 atmospheres of initial hydrogen pressure, while reductive elimination of the hydroxyl group takes place under similar conditions in the presence of dimethyl disulfide, thiophene, etc.

$$H_2O + RCH_3 \xleftarrow[\bar{S}]{Ni} RCH_2OH \xrightarrow{Ni} RH + CH_4 + H_2O$$

Evidence was given to show that the latter reaction proceeds *via* an ionic mechanism. It was suggested that a nickel catalyst possesses inherent acid properties and that sulfur compounds through their ability to poison the active contact sites of the nickel catalyst may accentuate the acid properties of the catalyst.

This study has been extended to olefinic hydrocarbons and has revealed that the presence of small amounts of sulfur compounds may also influence the hydrogenation of compounds such as 3,3-dimethylbutene or cyclohexene. These reactions were made in a flow type system at 300°, under 10 atmospheres of pressure using a ratio of hydrogen to hydrocarbons equal to 4:1 and nickel–kieselguhr as catalyst.

3,3-Dimethyl-1-butene.—In the absence of sulfur compounds this olefin yielded on hydrogenation hexanes composed of 93% 2,2- and 7% 2,3-dimethylbutane. When the hydrogenation was carried out, however, in the presence of a catalyst which was used previously for hydrogenation of compounds containing small amounts of thiophene, the extent of hydroisomerization of 3,3-dimethylbutene was greatly increased, and the product of the reaction contained 51% of 2,3-dimethylbutane. The hydroisomerization became the major reaction when 1% by weight of dimethyl disulfide was added to the 3,3-dimethylbutene. The hydrocarbons recovered consisted of 25% 2,2- and 75% 2,3-dimethylbutane (Table I).

TABLE I

EFFECT OF DIMETHYL DISULFIDE UPON THE HYDROGENATION OF 3,3-DIMETHYLBUTENE

The hydrogenation was carried out in a flow type apparatus at 300°, 10 atmospheres of pressure and using a hydrogen to 3,3-dimethylbutene ratio of 4:1.

Experiment	1	2	3
Catalyst	Ni–K[a]	Ni–K[b]	Ni–K[c]
Dimethyl disulfide, wt. %	0	0	1
Compn. of reacn. product, mole %			
2,2-Dimethylbutane	93	45	25
2,3-Dimethylbutane	7	51	75
3,3-Dimethylbutene		4	

[a] Fresh nickel–kieselguhr catalyst was used. [b] The catalyst was previously used in experiments in which a sulfur containing additive was present. [c] Catalyst from experiment 2 was used.

Cyclohexene.—Hydroisomerization of cyclohexene over nickel–kieselguhr catalyst under 10 atmospheres of pressure practically did not occur when the hydrogenation was carried out in the absence of sulfur compounds.[3] In the presence of 1% of dimethyl disulfide, however, 5% of cyclohexene was converted to methylcyclopentane. In the presence of larger amounts of disulfide 16% of methylcyclopentane was produced. The low yield of methylcyclopentane in the presence of 1% of dimethyl disulfide is probably due to the fact that fresh catalyst was used and that only partial deactivation of the catalyst occurred before a sample of the reacted product was withdrawn for analysis.

TABLE II

EFFECT OF DIMETHYL DISULFIDE UPON THE HYDROGENATION OF CYCLOHEXENE

The apparatus and experimental conditions were the same as described in Table I. The mole ratio of hydrogen to cyclohexene was 4:1. Nickel–kieselguhr was used as a catalyst.

Experiment	1	2	3
Dimethyl disulfide, wt. %	0	1	5
Compn. of reacn. prod., mole %			
Methylcyclopentane	1	5	15
Cyclohexane	99	95	81
Benzene			4

Discussion of Results.—It was found, as in the hydrogenolysis of alcohols,[2] that the presence of small amounts of sulfur-containing compounds can influence the type of activity of a nickel catalyst. In the presence of sulfur the nickel assumes acid characteristics, as shown by its hydroisomerization effect. The skeletal isomerization occurs most probably prior to hydrogenation, since the saturated hydrocarbons, such as cyclohexane or 2,2-dimethylbutane, under similar experimental conditions do not undergo isomerization. The probable mechanism of the hydroisomerization reaction is similar to that suggested for the reductive dehydroxylation of primary alcohols.[2]

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[1] On leave of absence from Laboratories de Recherches Purfina S. A. Bruxelles, Belgium, 1953–1954.

[2] H. Pines, M. Shamaiengar and W. S. Postl, THIS JOURNAL, **77**, 5099 (1955).

[3] H. Pines, A. Rudin, G. M. Bô and V. N. Ipatieff, *ibid.*, **76**, 2740 (1954).

Apparatus and Procedure.—The apparatus and procedure used were the same as those described previously.[4] The product from the reaction was distilled and the various fractions were analyzed by means of infrared spectroscopy.

Nickel-Kieselguhr.—This catalyst was obtained from Harshaw Chemical Co. in $^1/_8$ inch cylindrical pills. It contained 44% of nickel. Prior to use, it was reduced in a stream of hydrogen at 350°.

3,3-Dimethyl-1-butene was obtained by the pyrolysis of pinacolyl acetate. The latter was passed over glass wool in a nitrogen atmosphere at 400°.[5] It distilled at 41.2–41.7°, $n^{20}{}_D$ 1.3758.

(4) V. N. Ipatieff, F. J. Pavlik and H. Pines, This Journal, **75**, 3179 (1953).

(5) J. P. Wibaut and A. J. van Pelt, Jr., *Rec. trav. chim.*, **57**, 1055 (1938); **60**, 55 (1941).

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The Product Derived from the Cyclization of Triglycine Azide

By John C. Sheehan, Murray Goodman and Wallace L. Richardson

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In describing a new method for the synthesis of macrocyclic peptides we reported[1] the preparation from triglycine azide of a compound to which was assigned tentatively the structure cyclo-(triglycyl). Molecular weight determinations, which were incomplete at the time of the previous publication, have now shown the compound to be the dimer, cyclo-(hexaglycyl). The methods of freezing point depression and boiling point elevation failed to give reproducible molecular weight values, presumably due to the very low solubility of the compound under the conditions employed. An X-ray unit cell measurement[2] did not distinguish between the cyclo-(triglycyl) and cyclo-(hexaglycyl) possibilities.

However, by the method of isothermal distillation[3] using water as the solvent and dextrose as the standard, a molecular weight of 344 was obtained [calcd. for cyclo-(hexaglycyl) 342.31]. Very recently cyclo-(hexaglycyl) was reported[4] as a reaction product of the polymerization of N-carboxyglycine anhydride. At our request, Dr. C. H. Bamford kindly furnished a sample of his product for comparison. The infrared spectra (potassium bromide pellet) of the samples were superimposable over the range 2–15 μ. A mixed solubility study provided further evidence of identity. Dr. Bamford (private communication) informs us that his group has independently conducted a careful study of the nature of the products obtained by the two methods.

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(1) J. C. Sheehan and W. L. Richardson, This Journal **76**, 6329 (1954).

(2) The authors are indebted to Prof. D. P. Shoemaker of this Department for the X-ray analysis.

(3) N. D. Cheronis, "Micro and Semimicro Methods of Techniques of Organic Chemistry," Vol. VI, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1954, pp. 228–229.

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Heterocyclic Vinyl Ethers. X. Dialkoxy 1,4-Dioxanes and Alkoxy 1,4-Dioxenes[1]

By William E. Parham and Harry E. Reiff

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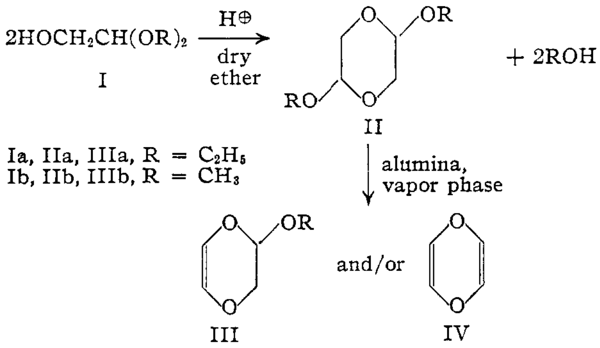
In paper III[2] of this series, a preparation of 1,4-dithiadiene was reported which involved the dealkoxylation of 2,5-diethoxy-1,4-dithiane, which was in turn prepared by the acid-catalyzed condensation of two molecules of mercaptoacetaldehyde diethyl acetal. An investigation of the analogous reactions in the oxygen series appeared to be of interest, and the following reaction sequence has been examined.



Ia, IIa, IIIa, R = C_2H_5
Ib, IIb, IIIb, R = CH_3

Hydroxyacetaldehyde diethyl acetal (Ia) has been prepared previously by reaction of ethanolic potassium hydroxide with bromoacetal at elevated temperatures.[3] However, variations in the published values for the refractive index and density of the product of this reaction[3b] indicated that varying amounts of ethoxyacetaldehyde diethyl acetal were present. Furthermore, we have observed that treatment of chloroacetal with alcoholic potassium hydroxide at elevated temperatures affords a 70% yield of ethoxyacetaldehyde diethyl acetal. Since hydroxyacetaldehyde dialkyl acetals, free of other acetals, were required for the preparation of the dialkoxydioxanes IIa and b, the following reactions leading to these acetals were investigated. Reaction of sodium benzyloxide (V) and bromoacetal (VIa) or dimethylchloroacetal (VIb) afforded the corresponding benzyloxyacetaldehyde dialkyl acetals (VII) in yields of 75–82%. The benzyloxyacetals were cleaved smoothly with sodium in liquid ammonia to give pure hydroxyacetals in good yield.

$$\underset{\text{V}}{C_6H_5CH_2ONa} + \underset{\text{VI}}{X\ CH_2CH(OR)_2} \longrightarrow$$

$$\underset{\text{VII}}{C_6H_5CH_2OCH_2CH(OR)_2} \xrightarrow[\text{liq. NH}_3\text{ then H}_2\text{O}]{\text{Na in}} C_6H_5CH_3 + \underset{\text{I}}{HOCH_2CH(OR)_2}$$

VIa, X = Br, R = C_2H_5; VIIa, R = C_2H_5
VIb, X = Cl, R = CH_3; VIIb, R = CH_3

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