funnel and washed with 0.1 N HCl, 5% sodium bicarbonate solution, and water, then dried over anhydrous sodium sulfate and evaporated to an orange-red sirup. Thin layer chromatography (silica gel, 2:1 benzene–petroleum ether) showed the presence of a substance of R_f 0.17 as major product besides desyl chloride (R_f 0.45) and benzoin (R_f 0.08) (see Table I). Treatment of this sirup with 180 mg. of sodium borohydride in 95% ethanol gave 1.18 g. (63.6%) of desoxybenzoin. Details of the substance of R_f 0.17 will be reported elsewhere.

The Clemmensen Reduction of 1,3-Diketones*[1]

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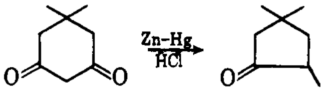
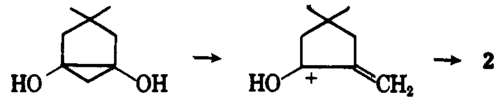
The use of amalgamated zinc in concentrated hydrochloric acid to reduce a ketone or aldehyde carbonyl to methylene is well known, and since the introduction of the method by Clemmensen[2] it has found wide use in organic chemistry.[3] The reaction has been used mainly to reduce monocarbonyl compounds, but the reduction of some diketones has also been reported. In 1933, Khuda[4] subjected 5,5-dimethylcyclohexane-1,3-dione (**1**) to this procedure and obtained, as one product, a monoketone different from the expected 3,3-dimethylcyclohexanone. Dey and Linstead[5] repeated this work and showed that the anomalous product was a ring-contracted ketone, 2,4,4-trimethylcyclopentanone (**2**).



1 **2**

Confirmation of this result was obtained by Khuda and Mukherji[6] who carried out an unambiguous synthesis of this five-membered ring ketone. Subsequently it was shown that another 1,3-diketone underwent rearrangement on Clemmensen reduction, 2,2,4,4-tetramethylcyclobutane-1,3-dione giving some 2,5-dimethylhexan-3-one.[7] A number of cases have been reported where 1,3-diketones have been reduced by the Clemmensen method to hydrocarbons, but unequivocal evidence for the structures of the latter is lacking.[3]

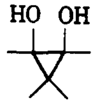
In a review of the Clemmensen reaction, Staschewski[8] proposed a mechanism for the rearrangement observed with 5,5-dimethylcyclohexane-1,3-dione. He postulated that the diketone adds two electrons and two protons to give a diradical which then, intramolecularly, forms a new carbon–carbon bond (**1** → **3**). In the acidic medium this intermediate undergoes a pinacol-type rearrangement (**3** → **4**), further reduction leading to the observed product **2**. It appears that this reaction is faster than the subsequent reduction of the monoketone, enabling the latter to be isolated in up to 50% yield.



3 **4**

We now present evidence to show that this rearrangement is a general one for the Clemmensen reduction of 1,3-diketones.

Pentane-2,4-dione gave 3-methylbutan-2-one as the sole ketonic product, gas chromatography demonstrating the absence of unrearranged pentan-2-one. On the mechanism developed above, it is not possible to distinguish between C-1 and C-3 of the starting material in the final product. However, by using 3,3-dimethylpentane-2,4-dione, the intermediate cyclopropanediol (**5**) may rearrange either by migration of the C-1 methyl group to give, finally, 2,4-dimethylpentan-3-one or by migration of the C-3 CMe$_2$ group to give, finally, 3,4-dimethylpentan-2-one (**6**). In fact **6** was shown to be the only monoketone present in the products.



5

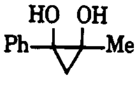
$\rightarrow$ Me·COCH(Me)·CHMe$_2$

6

1-Phenylbutane-1,3-dione (**7**) would form an unsymmetrical cyclopropanediol (**8**), and, if it rearranged by loss of the hydroxyl group on the carbon α to the phenyl group to form a benzylic carbonium ion, then the final product would be 3-phenylbutan-2-one. Loss of the other hydroxyl group would lead to 2-methyl-1-phenylpropan-1-one. In fact, only the former ketone was obtained and the isomeric one was shown to be absent. 2-Phenylbutane, the product of complete reduction of the rearranged ketone, was shown to be a minor product of this reaction.

PhCOCH$_2$COMe $\rightarrow$

7



8

The present results, taken with those obtained previously, offer strong support for the mechanism proposed[8] for the Clemmensen reduction of 1,3-diketones.

Experimental

Pentane-2,4-dione.—Pentane-2,4-dione (30 g., 0.30 mole) was added to zinc (200 g., 3.06 g.-atoms), previously amalgamated by the procedure of Martin[3] in 8 M hydrochloric acid (350 ml.), and the mixture was heated under reflux in a flask fitted with a short distillation column. Slow distillation was begun after a few minutes and continued until no more oily droplets passed over. Ether extraction of the distillate yielded a liquid which on distillation gave a forerun (b.p. up to 40°), probably hydrocarbons; a fraction, b.p. 93–96°, 9.1 g. (35%); and a fraction b.p. 130–145°, 0.27 g., chiefly pentane-2,4-dione, leaving a residue of 0.82 g. The second fraction was pure 3-methylbutan-2-one and showed identical boiling point, infrared and n.m.r. spectra, and gas chromatographic retention volume with those of an authentic sample.[9] The semicarbazone had m.p. and m.m.p.

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* To Professor Louis F. Fieser.

[1] A preliminary report has been published: N. J. Cusack and B. R. Davis, *Chem. Ind.* (London), 1426 (1964).

[2] E. Clemmensen, *Ber.*, **46**, 1837 (1913); **47**, 51 (1914); **47**, 681 (1914).

[3] E. L. Martin, *Org. Reactions*, **1**, 155 (1942).

[4] M. Qudrati-Khuda, *Nature*, **132**, 210 (1933).

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[6] M. Qudrati-Khuda and A. Mukherji, *J. Indian Chem. Soc.*, **23**, 435 (1946).

[7] H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

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[9] F. C. Whitmore, W. L. Evers, and H. S. Rothrock, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 408.

113-115° (lit.[10] m.p. 115°) and the 2,4-dinitrophenylhydrazone had m.p. and m.m.p. 120-121° (lit.[11] m.p. 122-123°). Pentan-2-one was shown to be absent by analytical g.l.c.

1-Phenylbutane-1,3-dione.—1-Phenylbutane-1,3-dione was reduced as described above for pentane-2,4-dione and yielded from ether a colorless liquid, b.p. 180-220°. Analytical gas chromatography showed the major product to be 3-phenylbutan-2-one (*ca.* 65% of distillate) together with 2-phenylbutane and two other compounds probably hydrocarbons. 2-Methyl-1-phenylbutan-1-one was shown to be absent. The total distillate yielded 3-phenylbutan-2-one semicarbazone, m.p. and m.m.p. 170-170.5° (lit.[12] m.p. 170-171°) and 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 125-126° (lit.[13] m.p. 125-126°). Authentic 3-phenylbutan-2-one was prepared from 1-phenylpropan-2-one by methylation with methyl iodide and aqueous sodium hydroxide.[13] 2-Phenylbutane was prepared from this by Wolff-Kishner reduction.

3,3-Dimethylpentane-2,4-dione.—3,3-Dimethylpentane-2,4-dione[14] (5 g.) was reduced as described above and yielded, on ether extraction, a colorless liquid, b.p. 130-180° (2.1 g.). Analytical gas chromatography showed that 3,4-dimethylpentan-2-one was the major product together with some starting material and a little low-boiling material, probably a hydrocarbon. 2,4-Dimethylpentan-3-one was shown to be absent. The total product on distillation gave 3,4-dimethylpentan-2-one, b.p. 135-138°. Authentic 3,4-dimethylpentan-2-one, prepared by methylation of 2-methylpent-2-en-4-one and subsequent hydrogenation,[15] had b.p. 136-138°, semicarbazone m.p. 113°.

Acknowledgment.—We acknowledge assistance from the Research Grants Committee of the New Zealand University Grants Committee.

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Imido Glycols as Stable Polar Liquid Phases in Gas Chromatography*

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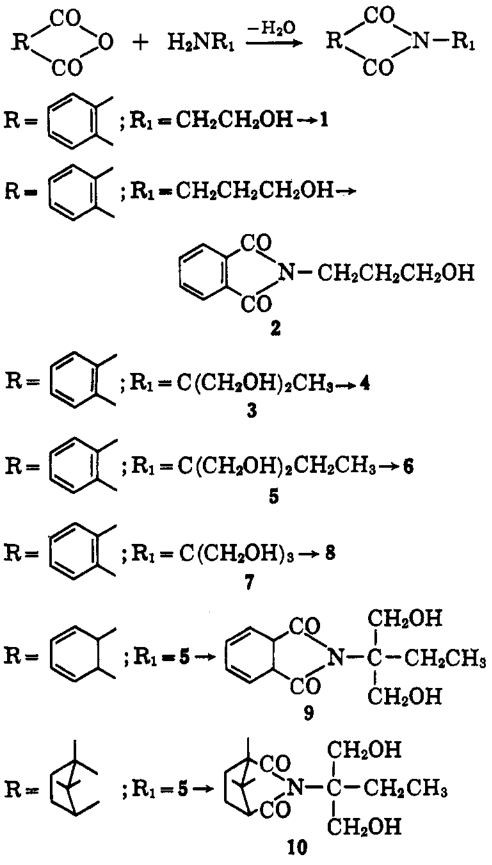
Effective gas chromatographic separation of polar compounds is intimately connected with the availability of high-boiling polar liquid phases. Conventional liquids, like polyethylene glycols and their esters, show considerable deterioration (aging) at useful column temperatures (around 150°). Unfortunately, as a rule, the more polar and suitable the liquids are (that is, the better the separations they permit as long as they are freshly prepared), the faster they deteriorate ("bleed"). In most of the cases the useful life span of such unstable columns is a few weeks or even less, and the specific retention (elution) time, so important for proper identification purposes, is no longer a constant but at best a relative criterion. In the search for temperature-stable high-boiling polar liquids we were guided by earlier observations in the preparation of N-vinyl monomers[1,2] that certain tertiary dicarboximides (**1**) represent compounds of remarkable stability against exposure to high temperatures.

At first, simple hydroxyalkylphthalimides were tried. The lower members of this series are crystalline sharp-melting compounds, one of them (**2**) not previously encountered in the literature. Unfortunately, the practical usefulness of the lower members as a chromatographic substrate is limited; this is partly due to their relatively high vapor pressure and tendency toward sublimation.

With the commercial availability of higher molecular weight and more polar amino glycols (**3**, **5**, and **7**),[3] certain imides can be prepared which overcome these problems (**4**, **6**, **9**, and **10**). Although these compounds have been prepared under milder conditions than the one (**4**) described earlier,[4] a proof of homogeneity of the compounds or the identification of their components could not be provided.



Inexplicably, possibly due to its high melting point, the condensation product with tris(hydroxymethyl)-aminomethane (**8**) was useless as a chromatographic liquid phase. Both the 2-methyl- and 2-ethyl-2-aminopropane-1,3-diols have given useful condensation products (**4** and **6**), and for its better resolving power we have preferred the liquid phase obtained with the 2-ethyl compound (**6**).

In gas chromatography of terpenes and terpenoids it is customary to blend a polar with a nonpolar liquid (50:50) in order to make the resulting column capable of resolving the mixture of polar compounds and hydrocarbons as well. With the inclusion of the condensation

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* To Professor Louis F. Fieser.

(1) W. E. Hanford and H. B. Stevenson (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,231,905 (1941); *Chem. Abstr.*, **35**, 3267^4 (1941); U. S. Patent 2,276,840 (1942); *Chem. Abstr.*, **36**, 4637^4 (1942); U. S. Patent 2,365,340 (1944); *Chem. Abstr.*, **39**, 4627^2 (1945); D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 911 (1947).

(2) One of the authors' (R. L. M.) unpublished results.

(3) Courtesy of the Commercial Solvents Corp.

(4) M. M. Sprung, *J. Am. Chem. Soc.*, **61**, 381 (1939).