Cyclization of 3-Methyl-3-(2′-isopropenylphenyl)butyronitrile.—The cyclization of 3-methyl-3-(2′-isopropenylphenyl)butyronitrile in polyphosphoric acid was carried out as previously described. The yield of ketone and lactam were found to be identical to that obtained in the Beckmann rearrangement of the parent oxime.

Cyclization of 3-Methyl-3-(2′-isopropenylphenyl)butyramide.—The cyclization of 0.10 g. of 3-methyl-3-(2′-isopropenylphenyl)-butyramide using the procedure described previously for 3-(2′-isopropenylphenyl)propionamide at 150–155° for 45 min. resulted in the isolation of the lactam, 2-aza-1,1,5,5-tetramethyl-3-benzosuberone, m.p. 144–145°.

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Notes

A Rapid, Precise Procedure for the Quantitative Determination of Unsaturation in Organic Compounds *via* Hydrogenation

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We wish to report a simple procedure which permits the rapid, quantitative determination of unsaturation in representative organic compounds. The method utilizes the new active platinum metal catalysts prepared by the *in situ* treatment of platinum metal salts with sodium borohydride,[1] the *in situ* generation of hydrogen from sodium borohydride, and a modification of the valve[2] which automatically introduces sodium borohydride solution into the reaction mixture as the hydrogenation is proceeding. With these modifications, hydrogenation[3] becomes a rapid, precise tool for the determination of unsaturation.

The apparatus is shown in Fig. 1. In this device, the buret ends in a capillary tube which dips into a mercury well to a depth sufficient to support the column of solution (sodium borohydride in ethanol). As hydrogen is utilized in the hydrogenation flask, the pressure drops 5 to 10 mm. below atmospheric, drawing a small quantity of the borohydride solution through the mercury seal, where it rises to the top of the mercury and runs into the flask through the small vent holes located just above the mercury interface. The acidic solution in the flask converts the borohydride into hydrogen and the resulting increase in pressure seals the valve. The addition proceeds smoothly and automatically to the completion of the hydrogenation, with the amount of borohydride solution corresponding quantitatively to the amount of unsaturated compound contained in the flask.

The procedure was tested by hydrogenating 20.0, 10.0, and 5.00 mmoles of[c] 1-octene, introduced as the pure liquid, and 5.00, 2.50, 2.00 and 1.00 mmoles of 1-octene, introduced as a standard solution in ethanol, using 1.00 *M*, 0.250 *M*, and 0.100 *M* sodium borohydride in ethanol. The procedure was extended to the hydrogenation of 4-methylcyclohexene, 1,5,9-cyclododecatriene, and ethyl oleate, as well as to a mixture of the above four unsaturated compounds. The results are summarized in Table I.

TABLE I

HYDROGENATION OF VARIOUS UNSATURATED COMPOUNDS

Compound	Amt., mmoles	$NaBH_4$ soln. *M*	Volume of $NaBH_4$ solution	Av.	F.S.E.[c]	Olefin found, mmoles
1-Octene	20.0[a]	1.00	4.95, 4.94, 4.90, 4.96, 4.95	4.94 ± 0.02	0.32	20.08 ± 0.020
	10.0[a]	1.00	2.46, 2.44, 2.48, 2.44, 2.42	2.45 ± 0.02	.16	9.96 ± 0.018
	5.00[a]	1.00	1.23, 1.22, 1.22, 1.24, 1.20	1.22 ± 0.02	.08	4.96 ± 0.016
	5.00[b]	0.250	4.57, 4.59, 4.62, 4.56 4.63	4.97 ± 0.03	.38	4.97 ± 0.030
	2.50[b]	.250	.27, 2.06, 2.24, 2.25, 2.25	2.26 ± 0.02	.19	2.45 ± 0.015
	1.00[b]	.250	0.92, 0.91, 0.90, 0.92, 0.91	0.91 ± 0.01	.08	0.99 ± 0.010
	2.00[b]	.100	4.31, 4.39, 4.30, 4.32, 4.30	4.32 ± 0.03	.25	1.98 ± 0.030
	1.00[b]	.100	2.18, 2.15, 2.20, 2.15, 2.20	2.18 ± 0.03	.13	1.00 ± 0.025
4-Methylcyclohexene	2.00[b]	.100	4.32, 4.35, 4.38, 4.36, 4.32	4.35 ± 0.03	.25	1.99 ± 0.025
1,5,9-Cyclododecatriene	0.67[b]	.100	4.32, 4.33, 4.37, 4.35, 4.35	4.34 ± 0.02	.25	1.99 ± 0.025
Ethyl oleate	2.00[b]	.100	4.35, 4.39, 4.32, 4.35, 4.37	4.36 ± 0.02	.25	2.00 ± 0.020
Mixture[d]	2.00[b]	.100	4.37, 4.39, 4.40, 4.37, 4.38	4.38 ± 0.10	.25	2.01 ± 0.012

[a] Introduced as the pure liquid. [b] Introduced as a 1.00 *M* solution in ethanol. [c] mmoles of hydrogen displaced by the volume of olefin or olefin solution introduced plus volume of sodium borohydride introduced (total volume in cc./25.0). [d] A mixture of 1-octene, 4-methylcyclohexene, 1,5,9-cyclododecatriene, and ethyl oleate, prepared by mixing aliquots of the 1 *N* ethanolic solutions.

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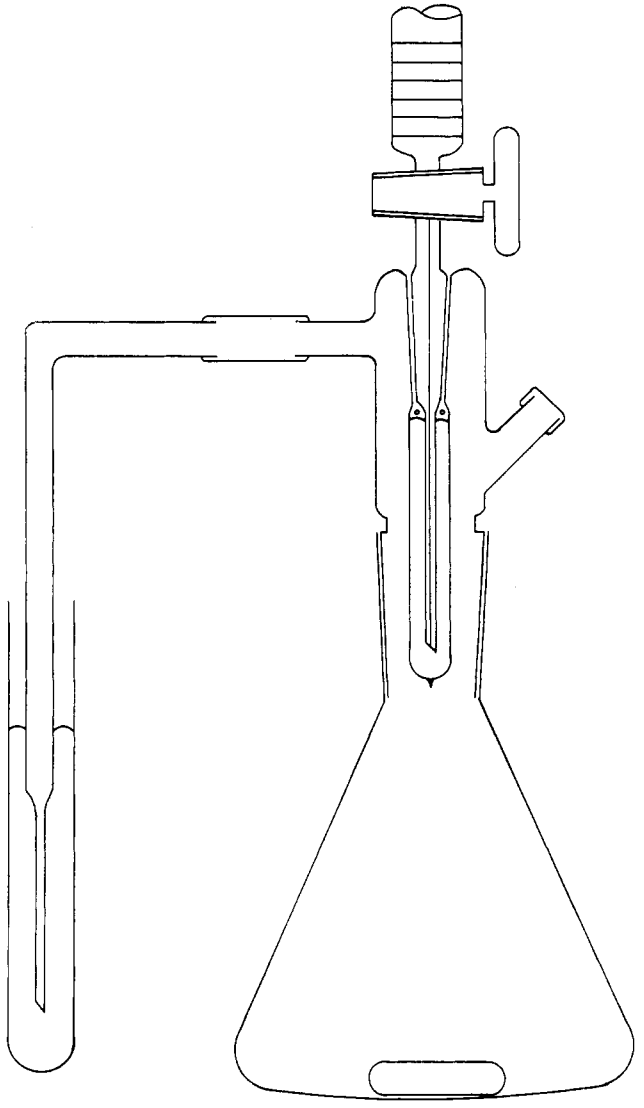

Fig. 1.—Apparatus for the quantitative hydrogenation of unsaturated compounds.

The precision and accuracy appear highly satisfactory It should also be pointed out that the five successive determinations were made consecutively with the same preparation of catalyst. Each determination required only 1–2 minutes for completion. Consequently, this apparatus and procedure appear to provide a highly convenient, precise analysis for unsaturation in organic compounds.

Experimental

Procedure.—A stock solution of sodium hydroxide in ethanol (0.100 *M*) was prepared by dissolving 4.00 g. of sodium hydroxide in 50.0 ml. of water and diluting to 1.0 l. with absolute ethanol. The standard sodium borohydride solution was prepared by adding 3.95 g. of sodium borohydride (Metal Hydrides Incorporated, 98%) to 100.0 ml. of this ethanolic solution and stirring magnetically until solution of the salt was complete. If the solution was not clear, it was filtered through a plug of glass wool. The solution was standardized by injecting 10.00 ml. with a hypodermic syringe into aqueous acetic acid and measuring the hydrogen evolved. The 0.250 *M* and 0.100 *M* sodium borohydride solutions were prepared by diluting aliquots of the 1.00 *M* solution with the sodium hydroxide–ethanol solution.

In the 125-ml. flask of the apparatus (Fig. 1) was placed 1.00 g. of Darco K-B carbon, 40.0 ml. of absolute ethanol, 1.00 ml. of 0.02 *M* chloroplatinic acid solution, and a Teflon-covered magnetic bar. The apparatus was assembled with a rubber stopple in the injection port. The flask was immersed in a beaker of water maintained at 25°. Injection of 5.00 ml. of 1.00 *M* sodium borohydride with a syringe into the vigorously stirred solution produced the catalyst. After about 1 min., 2.00 ml. of concentrated hydrochloric acid was injected, destroying the excess borohydride and providing a hydrogen atmosphere. A small quantity of 1-octene was injected to bring the apparatus to equilibrium.

The analysis was carried out by injecting either the pure liquid olefins or standard solutions of the olefin in ethanol with a syringe. Hydrogenation proceeded rapidly to completion. Generally, but 1 to 2 min. proved adequate for each individual determination. A total of 5 to 10 successive analyses could be carried out before the flask became inconveniently full.

In order to obtain the number of millimoles of double-bonds in the samples, it is necessary to add to the number of mmoles of "hydride" in the borohydride solution (1.00 *M* $NaBH_4$ = 4.00 *M* "hydride") the number of mmoles of hydrogen displaced by the volume of the sample introduced plus the volume of the borohydride solution used. Since 1 mmole of hydrogen at ordinary temperatures and pressures occupies a volume of very nearly 25 cc., this free space equivalent (F. S. E. of Table I) may be conveniently estimated by multiplying the sum of the added volumes by 0.04.

It should be pointed out that an alternative procedure in which hydrogen is generated in one flask and is utilized in a second provides a slightly modified method which may have advantages in some special cases.[2]

Presently we are exploring the applicability of this automatic hydrogenation procedure to the analysis of micro quantities of unsaturated compounds.

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Chelation as a Driving Force in Organic Reactions. V.[1] The Preparation of α-Nitro Esters through the Carboxylation of Nitroparaffins

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The synthetic utility of α-nitro esters dates almost from Steinkopf's[2] first synthesis of nitroacetic acid by the self-condensation of nitromethane. Reduction of the nitro group leads to α-amino esters,[3] reaction with Mannich bases provides a synthesis of δ-keto esters,[4] and treatment with sodium nitrite provides a synthesis of α-oximino esters.[5] However, the preparation of the nitro ester itself has not been simple, and, consequently, a number of techniques have been developed for their synthesis. Steinkopf used the nitration of diethyl methylmalonate in the preparation of α-nitropropionic acid.[6] Kornblum has developed a modification of the Victor Meyer reaction to convert α-halo esters to α-nitro esters.[7] The activity of the acidic α-hydrogen in ethyl nitroacetate has been utilized in a Michael addition to acrylonitrile and ethyl acrylate.[8]

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