pounds into line with the corresponding waters and ammonias.

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Chromatography of Some Common Indicators

BY J. V. KARABINOS[1] AND P. M. HYDE

Alumina,[2] calcium carbonate, talc, Super Cel and Hyflo Super Cel have been used successfully as adsorbents for the chromatography of coal tar dyes and indicators.[3] We wish to add to this list Silene EF[4] which has already found extensive use in the carbohydrate series.[5]

The relative degree of adsorption of the indicators on Silene EF–Celite 535[6] (5:1 by weight) was determined as follows. The indicator (0.75 mg.) dissolved in 0.4 ml. of 90% dioxane (90 ml. dioxane–10 ml. water) was put on a Tswett column (10 × 100 mm.) previously wetted with 0.5 ml. of the solvent and the indicator was developed with 5.0 ml. of 90% dioxane. The position of the colored zone was easily determined since the length of the column was calibrated in mm. (0, bottom; 100 mm., top). Checks were obtained in duplicate runs. Comparative data on the relative adsorption of the indicators on Silene EF–Alumina–Celite 535 (5:5:2 by weight) are also presented.

TABLE I

RELATIVE DEGREE OF ADSORPTION OF SOME INDICATORS

Indicator	Position of zone, mm. (color) Silene EF	Position of zone, mm. (color) Silene EF–Alumina
Aurin tricarboxylic acid, ammonium salt	99–100 (Br)	99–100 (Br)
Indigo carmine	99–100 (Bl)	99–100 (Bl)
Alizarin red S	98–100 (R)	98–100 (R)
Alizarin yellow R	98–100 (Y)	98–100 (Y)
Methyl violet	68–100 (Bl)	60–93 (Bl)
Dichlorofluorescein	91–96 (O)	97–98 (Y-O)
Congo red	85–90 (R)	97–100 (O)
Brom phenol blue	73–80 (P)	95–99 (P)
Brom cresol green	62–70 (Bl)	96–99 (Bl)
Chlor phenol red	60–70 (P)	95–98 (P)
Brom cresol purple	15–25 (P)	65–75 (P)
m-Cresolsulfonphthalein	15–25 (Y)	57–63 (O)
Methyl orange	5–20 (Y)	51–60 (Y)
Tropaeolin 00	8–18 (Y)	45–55 (Y)
o-Cresolphthalein	8–18 (Y)	47–55 (Y)
Thymol blue	0–10 (Y)	25–35 (Y)
Cresol red	8–15 (Y)	48–52 (Y)
Brom thymol blue	0–4 (Y)	0–2 (Y)
m-Nitrophenol	0	0
Phenolphthalein	0	0

It is interesting to note that the highly polar dyes, *e. g.*, the sodium salts are more strongly adsorbed.

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[1] Present address: Department of Chemistry, St. Procopius College, Lisle, Illinois.

[2] C. P. grade, J. T. Baker Chemical Company, Phillipsburg, New Jersey.

[3] P. Ruggli and P. Jensen, *Helv. Chim. Acta*, **18**, 624 (1934); **19**, 64 (1936); P. Ruggli and M. Stauble, *ibid.*, **23**, 689 (1940); H. H. Strain, THIS JOURNAL, **61**, 1292 (1939); W. Rieman, *J. Chem. Ed.*, **18**, 131 (1941).

[4] A commercial hydrated calcium silicate generously supplied by the Columbia Chemical Division, Pittsburgh Plate Glass Co., Barberton, Ohio.

[5] L. W. Georges, R. S. Bower and M. L. Wolfrom, THIS JOURNAL, **68**, 2169 (1946).

[6] Johns–Manville Co., New York, N. Y.

Preparation of Resacetophenone

BY JOSEPH R. KILLELEA AND H. G. LINDWALL

The zinc chloride method commonly employed for the preparation of resacetophenone[1] involves a vacuum distillation and yields 65% of colored product. Since the vacuum distillation of high-melting solids is a troublesome process, we have adopted a boron fluoride method which eliminates the necessity of the distillation and gives superior yields of colorless product. Details are given below.

A mixture of resorcinol, 55.0 g. (0.5 mole), acetic anhydride, 54.5 g. (50.0 ml., 0.53 mole) and commercial anhydrous ether, 75 ml., is saturated with gaseous boron fluoride in an ice-bath. The mixture is then stored in a refrigerator for ninety-six hours. The heavy, yellow crystalline mass is broken up with a glass rod and the contents of the flask transferred to a beaker containing 200 g. of crushed ice. The ether is distilled off on a water-bath or allowed to evaporate in a good hood. The light yellow solid is washed with cold water. It weighs 73.0 g. (96%) and melts at 138–142°. It may be recrystallized from 1200 ml. of boiling water (Norit), the recovery being 69.0 g. of colorless solid (91%) melting at 144–145°.

A mixed melting point of this product with a sample prepared by the zinc chloride method showed no depression. The dibenzoate, prepared by Baker's method[2] melted at 80–81° mixed with the dibenzoate prepared from Cooper's product, 80–81°.

The boron fluoride method exemplified above has been employed, with slight modifications, in this Laboratory for the preparation of other polyhydroxyacetophenones.

(1) Cooper, "Org. Syn.," **21**, 103 (1941).

(2) Baker, *J. Chem. Soc.*, 1384 (1933).

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Vanadium Oxide, a Hydrogenation Catalyst[1]

BY V. I. KOMAREWSKY, L. B. BOS AND J. R. COLEY

Vanadium oxide is widely used as an oxidation catalyst. It has also been reported to be an effective catalyst for the dehydrogenation of hydro-

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[1] Presented before the Division of Petroleum Chemistry at the Atlantic City Meeting of the American Chemical Society, April 14, 1947.

carbons,[2] the hydrogenolysis of phenols[3] and of aliphatic alcohols.[4]

In this work a direct hydrogenation of unsaturated hydrocarbons in the presence of vanadium oxide catalyst is described.

Experimental

Apparatus and Procedure.—The catalytic hydrogenation procedure employed consisted of passing a three to one (by volume) mixture of hydrogen and vaporized unsaturated hydrocarbon over a granular (8–10 mesh) catalyst bed (volume, 50 cc.) maintained at uniform temperature by an electrically heated furnace. The rate of passage of the reactants through the Pyrex glass or steel reaction tubes (i. d. 15 mm.) was varied in the range of 0.01 to 1.00 liquid space velocity. The methods of feeding the reactants and condensing and collecting the products were conventional for vapor phase catalytic procedure.

Catalysts.—The vanadium oxide–aluminum oxide (V_2O_5, 35%–Al_2O_3, 65%) catalyst was prepared by coprecipitation from solutions of sodium vanadate and aluminum nitrate. The precipitation was accomplished by the addition of a calculated amount of a sodium hydroxide–sodium vanadate solution to a well-cooled solution of aluminum nitrate. The composition of the catalyst was checked by chemical analysis.

Analysis of Products.—The per cent. unsaturation of the liquid products was determined by the bromine number method.[5] The gaseous products were analyzed by the Gockel method.[6] The per cent. of butadiene in the gaseous product was determined by the maleic anhydride method.[7] The percentage of conversion of benzene to cyclohexane was determined by the refractive index.

Discussion of Results

Olefins, diolefins and acetylene when subjected to the action of vanadium oxide–aluminum oxide (V_2O_5, 35%–Al_2O_3, 65%) catalysts at 400° and atmospheric pressure were readily hydrogenated. The per cent. hydrogenation of isobutylene, hexene-1 and octene-1 obtained was in excess of 95%.

The optimum temperature for the olefin hydrogenation procedure was found to be 400°, which corresponds closely to the optimum temperature for the activated adsorption of hydrogen on vanadium oxide, as presented by Griffith[8] (see Fig. 1).

The space velocity proved to be a critical variable for this reaction. An increase in liquid space-velocity in excess of 0.05 gave a sizeable decrease in the effectiveness of the hydrogenation at atmospheric pressure. However, it was found that the maximum allowable space velocity could be materially increased by operation under increased pressure. The limiting space velocity was increased to 0.25 by operation at 21 atmospheres pressure (Table I).

TABLE I

DATA ON THE HYDROGENATION OF OLEFIN HYDROCARBONS AT 400°

Reactant	Pressure, atm.	Liquid space velocity, hr.$^{-1}$	Per cent. hydrogenation
Isobutylene	1	0.046	98.6
Isobutylene	1	.150	60.2
Isobutylene	1	.345	15.0
Octene-1	1	.010	98.6
Octene-1	21	.25	94.9
Octene-1	21	.50	82.2
Octene-1	21	1.00	58.9

Butadiene was readily hydrogenated at 400° and atmospheric pressure. The reaction product consisted of *n*-butane, 77.1% and butadiene 22.9%. No butenes were detected in the product.

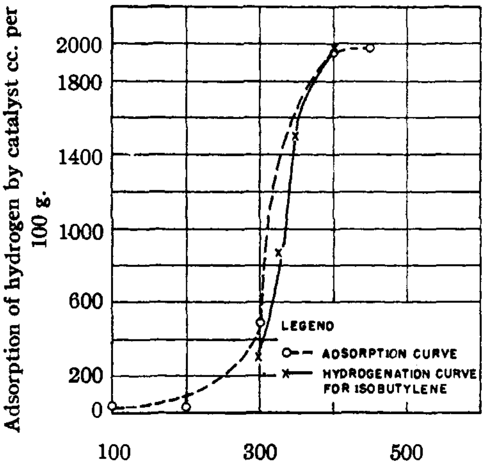

Fig. 1.—Comparison of hydrogenation curve for isobutylene and hydrogen adsorption curve—vanadium oxide catalyst.

Acetylene was hydrogenated successfully under the same reaction conditions. The reaction product consisted of 92.9% ethane, 0.2% acetylene and 6.9% ethylene.

Attempts to hydrogenate benzene at atmospheric pressure and 400° were unsuccessful. However, at 475° and 115 atmospheres, a yield of 27% cyclohexane was obtained. These particular high pressure experiments were carried out in a rotating autoclave.

An important feature of the vanadium oxide catalyst is its resistance to sulfur poisoning. The addition of 1% by weight of thiophene to hexene-1 and *t*-amyl mercaptan to octene-1 did not produce any noticeable decrease in the per cent. hydrogenation of either of these olefins. Sulfur analyses showed that 61.0% of the organic sulfur was removed by the catalytic hydrogenation for the hexene-1–thiophene mixture.

Vanadium oxide was shown to be an effective high temperature, low pressure, sulfur resistant

[2] Sachanen, "Conversion of Petroleum," Reinhold Publishing Corporation, New York, N. Y., 1940, p. 16.

[3] Griffith, "Mechanism of Contact Catalysis," Oxford University Press, London, 1936, pp. 17, 149.

[4] Komarewsky, Price and Coley, THIS JOURNAL, **69**, 238 (1947).

[5] Universal Oil Products Laboratory Test Methods for Petroleum and its Products, Universal Oil Company, Chicago (1940), method H-44-40.

[6] *Ibid.*, method G-84-40.

[7] *Ibid.*, method G-17-43.

[8] Griffith, "The Mechanism of Contact Catalysis," Oxford University Press, London, 1936, p. 186.

catalyst for the hydrogenation of unsaturated hydrocarbons.

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levo-2,3-Dinitroxybutane

BY A. F. McKAY, R. H. MEEN AND GEORGE F WRIGHT

In 1938, a diastereomeric mixture of 2,3-dinitroxybutanes was reported in 16% yield as one of the products arising from electrolysis of sodium methylethylacetate in aqueous solution of sodium nitrate.[1] Later sodium pentanoate was electrolyzed in the same way to yield a little of the nitrate ester, which was in the *dd, ll* form according to the dicarbanilide which it yielded after iron–acetic acid reduction.[2] Dinitroxybutane was finally reported in good yield from 2,3-butanediol, but the author does not specify the stereochemical configuration of this diol.[3]

In connection with studies involving plasticization of nitrocellulose, we wished to obtain 2,3-dinitroxybutane as a pure stereochemical compound. The availability of *levo*-butanediol through the courtesy of the Canadian National Research Council made this possible. The nitrate-esterification with mixed acid proceeded without incident. The crude product was sufficiently pure that its refractive index was not changed by subsequent fractional distillation. The distilled product was still clear after four years, when it gave an Abel Heat Test of two minutes at 100°. Its sensitiveness to impact between steel surfaces (glancing blow) was approximately the same as that of crystalline TNT. The compound was found to be a poor plasticizer for nitrocellulose of 13.1% nitrogen content.

Although the 2,3-butanediol from which this ester was prepared had a high *levo* rotation (−12.89°) the *levo* rotation of the resulting dinitroxybutane was less than 1°. This low rotation suggested that racemization might have occurred during nitration. This was found not to be the case. Catalytic reduction with the catalyst recommended by Kuhn[4] regenerated 2,3-butanediol with *levo* rotation of −12.90°.

Experimental

To a mechanically stirred solution of 228 cc. (5.4 moles) of 98% nitric acid in 219 cc. (3.79 moles) of 96% sulfuric acid was added dropwise, over one hundred and sixty minutes, 185.5 g. (2.06 moles) of *levo*-2,3-butanediol, b. p. 81.0° (18 mm.), $n^{25}\text{D}$ 1.4315, $[\alpha]^{20}\text{D}$ −12.89°. The reaction temperature was held at 0–5° during this addition and was maintained thus for a further fifteen minutes. The cold solution was then poured into 100 g. of ice and further diluted with 500 cc. of water. The oily layer was not freed completely from acid by washing with 1 liter of 2% sodium carbonate solution. The deacidification was therefore completed by further washing with 200 cc. of 2% aqueous ammonia and then with water until neutral to litmus.

The product was dried under 25-mm. pressure to weigh 337.5 g. or 91% of theoretical, $n^{20}\text{D}$ 1.4405. This refractive index was not changed by distillation at 99–100° (15 mm.) or 91.5° (10 mm.). *levo*-Dinitroxybutane melts at 0 to 4°. Other constants are: d^{20}_4 1.297; MR_D calcd. 36.94,[5] found 36.63; $[\alpha]^{20}\text{D}$–0.88.

Reduction of 2,3-Dinitroxybutane.—A 10% solution of 20 g. (0.11 mole) of 2,3-dinitroxybutane in absolute ethanol was reduced with 0.54 mole of hydrogen, initially at 500 lb. gage pressure, in presence of 0.5 g. of the palladium-on-charcoal catalyst recommended by Kuhn. It was necessary to heat the bomb to 48° in order to complete this reduction in seven hours. The hydrogenolysis was complete in twenty-two minutes when 2 g. of catalyst was used per 6 g. of ester. There was less evidence of ammonia formation in the quick reduction, but the reaction mixture became quite hot. The catalyst was filtered off and the filtrate distilled, finally under 14 mm. The yield of 2,3-butanediol distilling at 75–76° was 9.6 g. or 96% of theoretical. Its rotation was $[\alpha]^{20}\text{D}$° −12.90°.

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(1) F. Fichter and P. Suter, *Helv. Chim. Acta* **21**, 1401–1407 (1938).

(2) M. Rudin, *ibid.*, **25**, 636–640 (1942).

(3) L. J. DeKreuk, *Rec. trav. chim.*, **61**, 819–830 (1942).

(4) L. Kuhn, THIS JOURNAL, **68**, 1761–1762 (1946).

(5) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley & Sons Inc., New York, N. Y., 1945.

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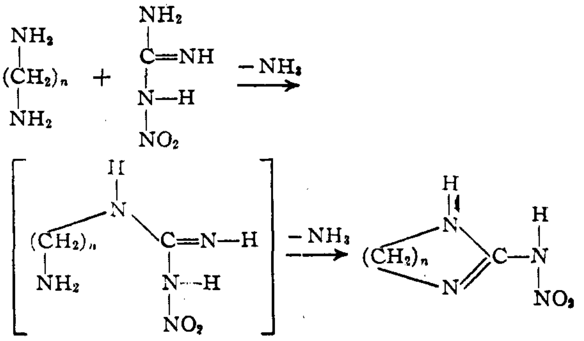
Preparation and Properties of 2-Nitramino-Δ²-1,3-diazacycloalkenes

BY A. F. McKAY AND GEORGE F WRIGHT

Davis and his co-workers[1,2] have shown that monoalkylamines react with nitroguanidine in aqueous solution to give the corresponding N-alkyl-N'-nitroguanidines. If these alkylnitroguanidines are treated with excess alkylamine then the nitramino group is replaced to give, among other products, the *sym*-dialkylguanidines.[3] One might then expect that, if nitroguanidine were treated with an alkyldiamine, both reactions would occur to give a cyclic derivative from which the nitramino group had been eliminated. However, the reaction follows an alternative course. Ammonia is, indeed, liberated by the reaction of the amino group in nitroguanidine with one of the amino groups in the diamine, but the second evidently adds to the imino group in the resulting



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(1) T. L. Davis and A. J. J. Abrams, *Proc. Am. Acad. Sci.*, **61**, 437 (1936).

(2) T. L. Davis and S. B. Luce, THIS JOURNAL, **49**, 2303 (1927).

(3) T. L. Davis and R. C. Elderfield, *ivid.*, **55**, 731 (1933).