NOTES.

Heat Deactivation of a Palladium Catalyst. By DAVID T. GIBSON.

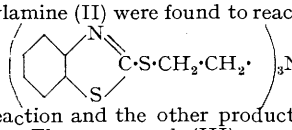
THE semi-hydrogenation of ethynyl*cyclo*hexanol was successfully effected by Cook and Lawrence (*J.*, 1938, 58) but not by Bergmann and Bergmann (*J. Amer. Chem. Soc.*, 1937, **59**, 1146) by interrupting the process when the required amount of hydrogen had been taken up. Since then Paul and Hilly (*Bull. Soc. chim.*, 1939, **6**, 218) and Thompson and Wyatt (*J. Amer. Chem. Soc.*, 1940, **62**, 2555) have shown that Raney iron reduces acetylenes to ethylenes and that the reaction stops there, but their experiments required high pressure, 50—100 atmospheres.

Bourgel (*Bull. Soc. chim.*, 1927, **41**, 1444) describes a palladium–starch catalyst which effects semi-hydrogenation at ordinary pressure, but his catalyst is somewhat troublesome to prepare, involving dialysis for several days.

The vinyl alcohol may be very conveniently isolated by using a modified Pd–$BaSO_4$ catalyst at atmospheric pressure. The ordinary catalyst (Weyl, *Methoden*, II, 270) is heated in air in an electric oven at 600° for 20 minutes. Using this catalyst, absorption of hydrogen by ethynyl*cyclo*hexanol is smooth until one molecule has been taken up when absorption ceases. Thus ethynyl*cyclo*hexanol (9 g.) dissolved in methanol (30 c.c.) with Pd–$BaSO_4$ (0·2 g.) took up 1610 c.c. of hydrogen (calc., 1620 c.c.) in 9 hours. Absorption was steady at 210 c.c./hour for the first seven hours falling abruptly to 20 c.c./hour after 9 hours. The product was shown to be essentially, vinyl*cyclo*hexanol by dehydration to vinyl-*cyclo*hexene followed by condensation with maleic anhydride to give the product described by Cook and Lawrence (*loc. cit.*) in good yield.

Catalysts heated at 700° and 800° effected no reduction at all; those at 300° allowed the reaction to proceed to completion (ethyl*cyclo*hexanol) without any appreciable break in the curve. —UNIVERSITY OF GLASGOW. [*Received, April 26th,* 1945.]

The Reaction Between 1-Thiolbenzthiazole and Trichlorotriethylamine. By RALPH F. REYNOLDS.

1-THIOLBENZTHIAZOLE (I) and ββ′β″-trichlorotriethylamine (II) were found to react with elimination of hydrogen chloride to give ββ′β″-tri(benzthiazole-1-thio)triethylamine,  , in approximately 30% yield. Over 80% of the 1-thiolbenzthiazole entered into reaction and the other products consisted of a small quantity of an orange-yellow solid together with much brownish oil. The compound, (III), was precipitated from its solution in concentrated acids by water, was recovered unchanged after refluxing for three hours with ethyl bromide in benzene solution, possessed none of the vesicant properties of (II) and exerted no apparent irritant action on the skin. It had only a very weak accelerating effect on the sulphur vulcanisation of Hevea rubber at temperatures up to 153°.

Compound (I), m. p. 176—178° was prepared by purifying the technical product and the hydrochloride of (II) had m. p. 130—131° (cf. Ward, *J. Amer. Chem. Soc.*, 1935, **57**, 914). All m. p.'s are uncorrected.

ββ′β″-Tri(benzthiazole-1-thio)triethylamine (III).—A 5% aqueous solution of ββ′β″-trichlorotriethylamine hydrochloride (100 c.c., 1 mol.) was added to a solution of 1-thiolbenzthiazole (10 g., 3 mols.) in 10% aqueous sodium hydroxide (30 c.c., 4 mols. NaOH) and the mixture refluxed for 15 mins. The yellowish-brown oil which separated solidified to a sticky yellowish mass which was washed with hot distilled water and dissolved either in hot acetone or hot alcohol–chloroform. From this solution a brownish oil separated and was removed. A further small quantity of oil separated on standing and this solidified to an orange-yellow solid (discarded) and a quantity of needle-shaped crystals. Repeated crystallisation of the latter from aqueous acetone finally gave (III) (3·7 g.) in pale yellow needles, m. p. 114·5—115·5° (Found: C, 54·5; N, 9·37; S, 31·6. $C_{27}H_{24}N_4S_6$ requires C, 54·3; N, 9·4; S, 32·2%: microanalysis by Drs. Weiler and Strauss, Oxford). The compound is readily soluble in chloroform, benzene, and dioxan in the cold, soluble in hot ethyl acetate, ligroin (b. p. 100—120°) and acetone, sparingly soluble in ethyl alcohol and practically insoluble in water and diethyl ether. Unreacted 1-thiolbenzthiazole was determined by acidifying the supernatant liquor from the reaction products together with the washings, filtering off and weighing.

ββ′β″-(Tribenzthiazole-1-thio)triethylamine platinichloride was obtained quantitatively by precipitating a solution of (III) (0·25 g.) in acetone (50 c.c.) with platinic chloride solution (5%, 3 c.c.). The buff-coloured precipitate was collected on a sintered glass crucible, washed with acetone–water (50 : 50) followed by acetone and dried to constant weight at 100° (Found: Pt, 12·12. $2C_{27}H_{24}N_4S_6,H_2PtCl_6$ requires Pt, 12·18%). Its m. p. is indefinite, darkening with decomposition at *ca.* 180°.

The author wishes to thank Miss K. M. Dyce-Sharp for assistance and the Directors of the Andre Rubber Co., Ltd., for permission to publish.—ANDRE RUBBER CO., LTD., KINGSTON BYPASS, SURBITON, SURREY. [*Received, May 16th,* 1945.]

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2 : 4-Dinitrophenylsemicarbazide. A Reagent for Aldehydes and Ketones. By (MISS) J. L. MCVEIGH and J. D. ROSE.

2 : 4-DINITROPHENYLSEMICARBAZIDE (I) was first described by Kniphorst (*Rec. trav. chim.*, 1925, **44**, 724), who prepared it from *N*-2 : 4-dinitrophenyl-*N*′-ethyl-*N*′-nitrourea and hydrazine hydrate. Barré and Piché (*Canad. J. Research*, 1941, **19**, 158) prepared (I) by heating 2 : 4-dinitrophenylurea with hydrazine hydrate in alcohol, and gave the m. p. as 178°; Kniphorst (*loc. cit.*) gave m. p. 195—197°. Kniphorst showed that (I) gave derivatives with acetone and with benzaldehyde, but no systematic attempt has been made to use this material as a reagent for the characterisation of aldehydes and ketones.

Compound (I) can be prepared readily by the interaction of *N*-2 : 4-dinitrophenyl-*N*′-nitrourea (Reudler, *Rec. trav. chim.*, 1914, **33**, 35) and hydrazine hydrate in alcoholic solution; the material has the constants recorded by Kniphorst. With aldehydes and ketones, (I) gives characteristic derivatives which are insoluble in water and very sparingly soluble in the common organic solvents. These derivatives may be prepared by addition of the carbonyl compound to a boiling saturated alcoholic solution of the reagent; under these conditions precipitation is usually immediate, but if slow, can be greatly accelerated by the addition of a few drops of hydrochloric acid. Alternatively, if it is necessary to prepare a quantity of a derivative, it is advantageous to use a solution of the reagent in hot glacial acetic acid in which it is easily soluble. A 0·1% solution of the *hydrochloride* of (I) in 2N-HCl may be used qualitatively to detect the presence of an aldehyde or ketone; with a 0·5% aqueous solution of acetone, a precipitate is formed in ten minutes, and with a 1·0% solution precipitation is immediate.

The 2 : 4-dinitrophenylsemicarbazones can be hydrolysed by boiling with 2N-sulphuric acid, and the ketone or aldehyde recovered by steam distillation.

The 2 : 4-*dinitrophenylsemicarbazones* of the following aldehydes and ketones have been prepared and are listed in the Table below :—

Aldehyde or ketone.	M. p. of deriv.	Formula.	Analysis. Required N%.	Calc. N%.
Formaldehyde	207° (decomp.)	$C_8H_7O_5N_5$	27·4	27·6
Acetaldehyde	225 ,,	$C_9H_9O_5N_5$	25·9	26·2
Crotonaldehyde	230 ,,	$C_{11}H_{11}O_5N_5$	24·2	23·9
n-Butyraldehyde	196 ,,	$C_{11}H_{13}O_5N_5$	23·6	23·7
*iso*Butyraldehyde	209	$C_{11}H_{13}O_5N_5$	23·4	23·7
Furfuraldehyde	227	$C_{12}H_9O_6N_5$	22·0	22·0
Benzaldehyde	232 *	$C_{14}H_{11}O_5N_5$	21·0	21·3
p-Dimethylaminobenzaldehyde	247 (decomp.)	$C_{16}H_{16}O_5N_6$	22·7	22·6
Anisaldehyde	248	$C_{15}H_{13}O_6N_5$	19·8 †	19·5
o-Chlorobenzaldehyde	248	$C_{14}H_{10}O_5N_5Cl$	18·8	19·2
Cinnamaldehyde	231 (decomp.)	$C_{16}H_{13}O_5N_5$	19·3	19·7
Methyl ethyl ketone	235 ,,	$C_{11}H_{13}O_5N_5$	24·1 †	23·7
Methyl *n*-propyl ketone	207 ,,	$C_{12}H_{15}O_5N_5$	23·2 †	22·7
Methyl *iso*butyl ketone	225 ,,	$C_{13}H_{17}O_5N_5$	22·0 †	21·7
Methyl *n*-hexyl ketone	192 ,,	$C_{15}H_{21}O_5N_5$	20·3	20·0
Ethyl acetoacetate	179	$C_{13}H_{15}O_7N_5$	19·7 †	19·8
5-Diethylaminopentan-2-one	175	$C_{16}H_{24}O_5N_6$	21·6	22·1
Di-*iso*propyl ketone	202—203	$C_{14}H_{19}O_5N_5$	21·0	20·8
*cyclo*Hexanone	234	$C_{13}H_{15}O_5N_5$	21·4	21·8
Benzoin	228	$C_{21}H_{17}O_6N_5$	16·5 †	16·1
Chalkone	226	$C_{22}H_{17}O_5N_5$	16·0	16·2
Benzylideneacetone	246	$C_{17}H_{15}O_5N_5$	18·7	19·0
Acetophenone	245 (decomp.)	$C_{15}H_{13}O_5N_5$	20·6	20·4
Deoxybenzoin	228	$C_{21}H_{19}O_5N_5$	16·8	16·7

* Kniphorst (*loc. cit.*) gives 223°.

† Recrystallised from dioxan. Nitrogen found on samples dried *in vacuo* at 110°.

For recrystallisation of the semicarbazones, it is advisable to avoid ethers as solvents. From dioxan, many of the substances retain solvent of crystallisation which adheres tenaciously and which is removed completely only on prolonged heating at 110° under reduced pressure.

2 : 4-*Dinitrophenylsemicarbazide* (I).—To hydrazine hydrate (150 g. of 50% w/w aqueous solution) in boiling ethanol (2 l.), *N*-2 : 4-dinitrophenyl-*N'*-nitrourea (Reudler, *loc. cit.*) (200 g.) was added during ¾ hr. Each addition caused vigorous effervescence (nitrous oxide) and, after 30 minutes crystals of the semicarbazide began to separate. When the addition was complete, the mixture was refluxed on the steam bath for one hour, cooled to 10° and the yellowish-brown crystals collected, washed with a little alcohol and dried (143 g.). Recrystallised from alcohol, it formed orange-yellow needles, m. p. 195—196° (decomp.). The *hydrochloride*, from alcohol, had m. p. 202—203° (Found : N, 25·1. $C_7H_7O_5N_5$,HCl requires N, 25·2%).

Benzaldehyde-2 : 4-dinitrophenylsemicarbazone.—The details of the preparation of this are given as an example of the use of the reagent. To a solution of 2 : 4-dinitrophenylsemicarbazide (0·31 g.) in boiling alcohol (40 c.c.) were added benzaldehyde (0·15 g. ; *ca.* 1 mol.) and one drop of concentrated hydrochloric acid. The mixture was boiled for 5 minutes, during which yellow crystals began to separate, and cooled to 10°. The yellow needles (0·31 g.) were collected, washed with alcohol (5 c.c.), dried, and had m. p. 232° (decomp.), unchanged by recrystallisation from chlorobenzene (Kniphorst, *loc. cit.*, gives m. p. 223°) (Found : N, 21·0. Calc. for $C_{14}H_{11}O_5N_5$: N, 21·3%).

Analyses by Mr. E. S. Morton. M. p.'s are uncorrected.—RESEARCH LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES LTD., BLACKLEY, MANCHESTER, 9. [*Received, June 13th*, 1945.]

β-(N-Dichloro)aminoethyl Hydrogen Sulphate (Sodium Salt). By K. H. PAUSACKER.

IT is claimed (I. G. Farbenind. A.-G., B.P. 427,943; *Chem. Abs.*, 1935, **29**, 6772), that certain aminosulphonic acids and the sulphuric acid esters of various amino-alcohols can be chlorinated, in the presence of anhydrous sodium acetate in acetic acid medium, to form *N*-chloro-substituted products. The formulæ ascribed to these substances are O←$NCl_2R{\cdot}X$ and O←NClR'R·X where X stands for either $-SO_3H$ or $-O{\cdot}SO_3H$.

The reaction using β-aminoethyl hydrogen sulphate (I) has been examined, and the product isolated was found to be the *sodium salt* of *β-(N-dichloro)aminoethyl hydrogen sulphate* (II).

The conditions employed were almost the same as those described in the above patent, with the exception that three times as much anhydrous sodium acetate (3·08 mols. per mol. of I) was used. It was found that the lower amount, being insufficient to react with the hydrogen chloride formed, was unsatisfactory

$$\underset{\text{(I.)}}{H_3\overset{+}{N}{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}\overset{-}{SO_3}} + 2Cl_2 + 3CH_3{\cdot}CO_2Na \longrightarrow \underset{\text{(II.)}}{Cl_2N{\cdot}CH_2{\cdot}CH_2{\cdot}OSO_3Na} + 2NaCl + 3CH_3{\cdot}CO_2H$$

Compound (I) (70 g.) was mixed with anhydrous sodium acetate (125 g.) and glacial acetic acid (490 c.c.). The mixture was vigorously stirred, and chlorine passed through it (1·5 hours) until the solution had a permanent yellow colour. The temperature was kept below 40° C. Dry air was then passed through the mixture to drive off excess chlorine, and the solid filtered and washed with a little absolute alcohol [151 g.; available chlorine content (av. Cl), 35·4%]. The filtrate yielded a further amount of solid by the addition of benzene (15 g. ; av. Cl, 44·6%). This corresponds to an 86% yield of (II).

The pure compound (II) was obtained by extracting the combined solids with absolute methanol at 50—60° (Found : Na, 9·76; av. Cl, 60·5%. $C_2H_4O_4NCl_2SNa$ requires Na, 9·90; av. Cl, 61·1%). It was a white crystalline solid readily soluble in water, and fairly stable in the dry state, although readily decomposed by boiling alcohol or water.

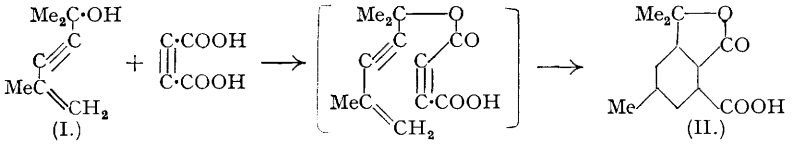
The author wishes to thank the Chemical Defence Board, Melbourne, for permission to publish these results.
UNIVERSITY OF MELBOURNE. [*Received, July 11th*, 1945.]

Formation of Phthalides by the Diels–Alder Reaction. By A. W. JOHNSON.

ACCORDING to recent papers of Heilbron, Jones and their co-workers (this vol., pp. 84, 88, 90) substituted tetrahydrophthalides may be obtained by Diels–Alder additions of conjugated diene alcohols to maleic anhydride.

A very similar reaction has been observed when the conjugated enyne alcohol 2 : 5-dimethylhexa-5-en-3-yn-2-ol (I) was added to acetylenedicarboxylic acid in benzene or ethyl acetate solution, 3 : 3 : 5-*trimethylphthalide*-7-*carboxylic acid* (II) being obtained. An attempted addition of 2 : 5-dimethylhexa-1 : 5-dien-3-yne (III; Mitchell and Marvel, *J. Amer. Chem. Soc.*, 1933, **55**, 4277) to acetylenedicarboxylic acid by heating the reactants at 140° in a sealed tube was unsuccessful, although a similar addition of (III) to maleic anhydride under these conditions has been reported (Butz, Gaddis, Butz and Davis, *J. Org. Chem.*, 1940, **5**, 386) and confirmed. Ethylenic compounds in general appear to undergo Diels–Alder additions with greater ease than their acetylenic analogues (cf. Sargent, Buchmann and Farquhar, *J. Amer. Chem. Soc.*, 1942, **64**, 2692).

It is therefore suggested that esterification is the primary reaction in the Diels–Alder addition of conjugated diene and enyne alcohols to maleic anhydride or acetylenedicarboxylic acid, and is followed by ring closure, *e.g.*



(I.) (II.)

$CH_2{:}CMe{\cdot}C{:}C{\cdot}CMe{:}CH_2$ (III.) $MeCH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}OCH_2{\cdot}C{:}CH$ (IV.) $MeCH(OH){\cdot}CH{:}CH{\cdot}C{:}CH$ (V.)

All attempts to cyclise *propargyl sorbate* (IV) by heating alone or in the presence of iodine have been unsuccessful, as was an attempt to obtain a phthalide by the addition of 3-hexen-5-yn-2-ol (V; Jones and McCombie, *J.*, 1943, 261) to acetylenedicarboxylic acid. The presence of a free ethinyl group in either of the reactants therefore appears to decrease the ease of cyclisation.

3 : 3 : 5-*Trimethylphthalide*-7-*carboxylic Acid.*—2 : 5-Dimethylhexa-5-en-3-yn-2-ol (2 g.; Nazarov, *Chem. Abstracts*, 1939, **33**, 5682) and acetylenedicarboxylic acid (1·8 g.) in benzene (15 c.c.) were refluxed for 2 hours. The product was cooled, extracted with 2N sodium hydroxide solution (3 × 10 c.c.) and the alkaline extract acidified. The product was separated and after two crystallisations from benzene–ligroin (b. p. 60—80°) it was obtained as colourless plates (3·0 g.; 79%), m. p. 159—160° (Found : C, 65·65; H, 5·2; equiv. (titration), 222. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·4%; equiv., 220). The product absorbed no hydrogen in the presence of Adams's platinum catalyst.

Propargyl Sorbate.—Propargyl alcohol (1 g.) was added to a solution of sorboyl chloride (2·4 g.; Staudinger and Schneider, *Ber.*, 1923, **56**, 710) in dry pyridine (3 c.c.). The mixture rapidly darkened and external cooling was necessary. After standing at room temperature, the mixture was heated at 60° for 1 hour, cooled and made alkaline with 2N sodium hydroxide. The product was extracted with ether and the ethereal extract washed, dried and the solvent removed. Distillation of the residue gave *propargyl sorbate* as a pale yellow oil, b. p. 57°/0·07 mm.; $n_D^{24°}$ 1·5174 (Found : C, 71·8; H, 6·6. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). The ester, on treating with ammoniacal silver nitrate, gave a white insoluble silver derivative which exploded on heating. On standing in air, propargyl sorbate is converted to a yellow resin after a few days.—RESEARCH LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES LIMITED, BLACKLEY, MANCHESTER, 9. [*Received, July 13th,* 1945.]

The Preparation of Olefins from Aldehydes and Ketones. By R. H. GRIFFITH.

ALTHOUGH the conversion of aldehydes and ketones to olefins can be effected by the two-stage process through the intermediate form of the alcohol, the direct hydrogenation to the hydrocarbon in good yield has not been described previously. Olefins have now been obtained by passing the vapours of aldehydes and ketones together with an excess of hydrogen, over a molybdenum oxide catalyst at 400°. The method appears to be of general application, but only a few examples have been examined in detail; these have given rise to heptene-1 from heptaldehyde, heptene-3 from dipropyl ketone, and styrene from acetophenone.

The catalyst was prepared from powdered molybdic acid, either by making into a paste with water, extruding into rods of $\frac{1}{8}$ in. diam. and breaking these into short lengths, or by compression into large cakes in a hydraulic press at about 500 atms. pressure, and breaking into pieces of suitable size. The material was dried at 100° and heated in a stream of hydrogen at 400° for 2 hours.

To a stream of hydrogen at 200 c.c./min., the liquid aldehyde or ketone was added from a saturator immersed in a thermostat at such a rate that about ten molecules of hydrogen accompanied each organic molecule. The mixture then entered an electric furnace in which 20 c.c. of catalyst were heated to the desired temperature; a thermocouple was embedded in the catalyst. The products leaving the reaction tube were cooled in ice and, when necessary, by solid carbon dioxide–acetone. In later experiments, liquid was added from a constant head device by displacement with mercury, at rates up to 30 c.c./hour. The volume of product, including that of water formed, was approximately the same as that of the feed.

The degree of conversion to the hydrocarbon depends on the precise throughput and temperature employed, but it is generally desirable to work under conditions which leave some 30—40% of aldehyde or ketone unchanged or else hydrogenation of the double bond begins to be noticeable and the hydrocarbon products contain appreciable amounts of paraffins.

After separation of water, the mixture was examined by fractionation in a small column with an efficiency of about 12 theoretical plates, followed by determination of refractive index and density. The table shows the results obtained under conditions where the yield of olefin was about 60% of theory, in comparison with established values for pure hydrocarbons recorded in *Physical Constants of the Principal Hydrocarbons*, Doss (1939).

		B. p. /760 mm.		$d_4^{20°}$.		$n_D^{20°}$.	
Original substance.	Product.	Obs.	Rec.	Obs.	Rec.	Obs.	Rec.
Di-*n*-propyl ketone ...	Heptene-3	94°	95·9°	0·7044	0·7043	1·4030	1·4090
Heptaldehyde	Heptene-1	94	94·9	0·7000	0·6993	1·4008	1·3999
Acetophenone	Styrene	142—146	143	0·9000	0·9038	1·5370	1·5440

The evidence indicates the presence of some 10—15% of ethylbenzene in the styrene, but shows that the two heptenes were practically free from paraffin. These conclusions were confirmed by bromine absorption results.

Qualitative experiments were also carried out with di*iso*propyl ketone and ethyl propyl ketone, which gave mixtures of olefins in the expected boiling point ranges.—THE FULHAM LABORATORY, THE GAS LIGHT AND COKE COMPANY, KING'S ROAD, S.W. 6. [*Received, July 17th,* 1945.]