was removed which on recrystallization from water melted with decomposition at 152–153°. This acid was converted into its anhydride in the same way as the acid obtained from Bruson's hydrochloride. The specimens of this anhydride from both sources melted without decomposition at 77.5–78.5°, alone and when mixed.

Preparation of the Acid Anilide and Phenylimide of the Synthetic β-Anhydride.—On addition of 0.1 g. of the anhydride dissolved in 1 cc. of benzene to 0.4 cc. of aniline a precipitate formed rapidly. This was filtered, washed with benzene and recrystallized twice from acetonitrile. It melted at 157.5–158°.

Anal. Calcd. for $C_{14}H_{17}O_3N$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.86; H, 6.58; N, 4.98.

The acid anilide was heated in a metal bath at 170° for five minutes. Steam was evolved and, on cooling, the sample solidified. It was crystallized three times from water–ethanol and melted at 169–170°. On resolidification, there was no change in melting point.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 74.66; H, 6.26; N, 5.81. Found: C, 74.28; H, 6.02; N, 5.37.

Mixed Melting Points.—The phenylimide of the anhydride from Bruson's compound, made in the same way, melted at 169–170°. There was no depression in a mixed melting point with the synthetic phenylimide.

Summary

The addition of strong acids, or the acid-catalyzed hydration, of dicyclopentadiene involves a normal Wagner–Meerwein rearrangement to yield derivatives of the *exo*-isomer of dihydrodicyclopentadiene and requires no modification of the current ionic interpretation of that rearrangement. This conclusion has been established by the oxidation of the "dihydro-*nor*-dicyclopentadiene" of Bruson and Riener[1] to the *exo-cis*-3,6-endomethylenehexahydrophthalic acid of Alder and Stein.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 24, 1945

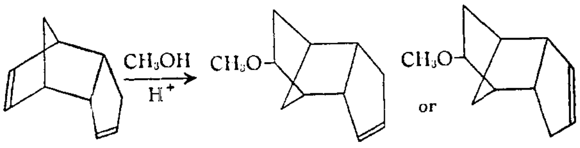
[CONTRIBUTION FROM RESINOUS PRODUCTS & CHEMICAL CO. AND ROHM AND HAAS CO., INC.]

The Chemistry of Dicyclopentadiene. III. Addition of Alcohols and Phenols

BY HERMAN ALEXANDER BRUSON AND THOMAS W. RIENER

When methanol reacts with dicyclopentadiene in the presence of an acidic catalyst such as sulfuric acid or boron trifluoride, an unsaturated methyl ether, $CH_3—O—C_{10}H_{13}$, is obtained which possesses an intense fragrant odor. The same ether is formed by warming methyl iodide with the sodium alcoholate of the acid catalyzed hydration product of dicyclopentadiene, previously referred to as hydroxy-dihydro-*nor*-dicyclopentadiene.[1] The latter has recently been shown by Bartlett and Schneider,[2] to be the *exo*-isomer of hydroxy-dihydro-dicyclopentadiene. Thus the same type of *endo–exo* addition–rearrangement involved in the acid-catalyzed reaction of dicyclopentadiene with water and with organic acids, occurs also with alcohols.

In accordance with Bartlett and Schneider's formulation for the rearrangement, the addition of methanol to dicyclopentadiene may be written as follows (assuming that the remaining double bond in the cyclopentene ring does not wander).



The residual double bond in the methoxy-dihydro-*exo*-dicyclopentadiene although quite inert toward the addition of a second molecule of methanol does, however, add halogen. Chlorine, for example, readily combines with methoxydihydro-*exo*-dicyclopentadiene to give the corresponding dichloro derivative.

In the same manner, it is possible to add a variety of other alcohols or hydroxy compounds to dicyclopentadiene to form the corresponding ethers of hydroxy-dihydro-*exo*-dicyclopentadiene. The ethers derived in this way from the lower aliphatic alcohols (ethyl, isopropyl, allyl, butyl) also possess strong floral odors. Other alcohols which add to dicyclopentadiene with *endo–exo* rearrangement of the ring system include the halogenated alcohols, nitro-alcohols, cyano-alcohols, hydroxycarboxylic acid esters and polyhydric alcohols, as shown in Table I. In the latter case mono- or poly-ethers are obtained depending upon the conditions.

Those ethers of hydroxy-dihydro-*exo*-dicyclopentadiene which possess at least two double bonds in the molecule as for example the allyl ether $C_3H_5—O—C_{10}H_{13}$, the ethylene glycol di-ether $C_{10}H_{13}—O—CH_2CH_2—O—C_{10}H_{13}$, the diethylene glycol di-ether $C_{10}H_{13}—O—C_2H_4—O—C_2H_4—O—C_{10}H_{13}$, and the ether ester of lactic acid $CH_3—CH(O—C_{10}H_{13})COO—C_{10}H_{13}$ or of glycolic acid $C_{10}H_{13}—O—CH_2COO—C_{10}H_{13}$, rapidly absorb oxygen from the air particularly in the presence of siccatives such as manganese or cobalt naphthenate to give hard, insoluble, varnish-like films, behaving in this respect like drying oils. They can also be polymerized by heating with peroxides to viscous autoxidizable oils.

Similar drying properties were shown by di-(dihydro-*exo*-dicyclopentadienyl) ether[3] $C_{10}H_{13}—O—C_{10}H_{13}$ obtained by adding hydroxy-dihydro-*exo*-dicyclopentadiene in the presence of sulfuric acid,[1] to dicyclopentadiene.

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(1) Bruson and Riener, THIS JOURNAL, **67**, 723, 1178 (1945).

(2) Bartlett and Schneider, *ibid*, **68**, 6 (1946).

(3) Previously referred to as "di-(dihydro-*nor*-dicyclopentadienyl) ether" in reference 1.

TABLE I

ETHERS OF HYDROXY-DIHYDRO-*exo*-DICYCLOPENTADIENE, R—O—$C_{10}H_{13}$

Value of R	M. p., °C.	Boiling point		Formula	Analyses, %			
		°C.	Mm.		Calcd. C	Calcd. H	Found C	Found H
CH_3—		95–96	13	$C_{11}H_{16}O$	80.40	9.75	80.31	9.79
C_2H_5—		104–105	12	$C_{12}H_{18}O$	80.89	10.11	80.47	10.12
$(CH_3)_2CH$—		110–111	12	$C_{13}H_{20}O$	81.24	10.41	80.89	10.65
$CH_2{=}CH{-}CH_2$—		117–118	11	$C_{13}H_{18}O$	82.10	9.47	81.62	9.45
$CH_3CH_2CH_2CH_2$—		129–131	11	$C_{14}H_{22}O$	81.55	10.67	81.02	10.77
$C_6H_5CH_2$—		160–162	4	$C_{17}H_{20}O$	85.00	8.33	84.79	8.35
C_6H_{11}—		115–116	0.45	$C_{16}H_{24}O$	82.76	10.34	82.85	10.48
$C_{10}H_{13}$—O—CH_2CH_2—		189–190	.45	$C_{22}H_{30}O_2$	80.98	9.20	80.77	9.44
HO—CH_2CH_2—O—CH_2CH_2—		144–146	.65	$C_{14}H_{22}O_3$	70.58	9.24	70.90	9.30
NC—CH_2CH_2—		173–174	13	$C_{13}H_{17}NO$	76.84	8.37	76.50	8.22
					N, 6.40		N, 6.74	
$ClCH_2CH_2$—		143–144	13	$C_{12}H_{17}ClO$	67.77	8.00	67.70	8.09
					Cl, 16.70		Cl, 16.30	
O_2N—$C(CH_3)_2$—CH_2—		136–137	0.38	$C_{14}H_{21}NO_3$	66.93	8.36	67.28	8.10
					N, 5.57		N, 5.31	
$(ClCH_2)_2CH$—		140–141	2	$C_{13}H_{18}OCl_2$	Cl, 27.20		Cl, 26.92	
C_6H_5—	71	140–150	1	$C_{16}H_{18}O$	84.95	8.00	85.30	7.97
α-$C_{10}H_7$—	69	210–220	2	$C_{20}H_{20}O$	86.96	7.25	86.40	7.76
p-C_6H_5—C_6H_4—	119	225–230	2	$C_{22}H_{22}O$	87.41	7.28	86.88	7.35
p-C_6H_{11}—C_6H_4—	60	212–216	2	$C_{22}H_{28}O$	85.71	9.09	85.41	9.27
p-Cl—C_6H_4—	55	165–175	2–3	$C_{16}H_{17}ClO$	Cl, 13.61		Cl, 13.50	
p-Br—C_6H_4—	72	190–195	3	$C_{16}H_{17}BrO$	Br, 26.21		Br, 26.52	

Phenols also add to dicyclopentadiene in the presence of sulfuric acid or boron trifluoride as catalysts to yield aryl ethers of hydroxy-dihydro-*exo*-dicyclopentadiene. These are well defined, in many cases crystalline compounds, in contrast to the resinous products described by other workers.[4] They are listed in Table I.

Experimental

The general procedure for treating hydroxy compounds with dicyclopentadiene consisted in gradually adding the dicyclopentadiene to a stirred solution of the acidic catalyst and the alcohol or phenol at room temperature. Typical catalysts used were concentrated 95–98% sulfuric acid, or the etherates of boron trifluoride, namely, $BF_3{\cdot}O(C_2H_5)_2$ or $BF_3{\cdot}O(C_4H_9)_2$. The quantity of catalyst used was varied from about 10 mole per cent. to about 25 mole per cent. of the weight of the dicyclopentadiene. In some cases particularly with chloro-alcohols or nitro-alcohols the reactions are strongly exothermic and care should be taken by adjusting the rate of addition and cooling, or by using an inert solvent (ethylene dichloride), that they do not get out of hand. After the initial reaction had subsided, the mixtures were heated two to six hours on a steam-bath. The dark oils thus obtained were then washed with water followed by a wash with dilute soda or sodium hydroxide solution and another wash with water. In some cases the oils were so thick that they were taken up in a solvent such as ethylene dichloride or toluene to thin them for easier washing. The washed oils were then dried and distilled *in vacuo*.

Methoxy-dihydro-*exo*-dicyclopentadiene.—To 240 g. of methanol cooled in an ice-bath, 100 g. of 98% sulfuric acid was added dropwise while the reaction mixture was stirred and maintained at a temperature between 5 and 20°. Dicyclopentadiene (528 g.) was then added gradually and the mixture was heated and stirred on a steam-bath, under reflux, for three and one-half hours. The product was poured into 1000 cc. of water, and the oil layer was separated. It was taken up in toluene and washed with water and soda solution, dried and distilled *in vacuo*. The product distilled at 80° (7 mm.) as a colorless oil having a powerful floral odor. The yield was 458 g. or 70% based on the dicyclopentadiene. Upon redistillation it boiled at 95–96° (13 mm.) or 217° at 757 mm. and had the following constants: n^{25}D 1.4961; d^{25}_4 1.0082; iodine no. 160 (theory 155) (for analysis see Table I).

The same compound was obtained by heating 45 g. of hydroxy-dihydro-*exo*-dicyclopentadiene[1] with 6.9 g. of sodium in 100 g. of benzene and treating the sodium alcoholate thus formed with 42.6 g. of methyl iodide for four hours under reflux on a steam-bath. The product obtained was washed, dried and distilled *in vacuo* to yield 20 g. of pure methoxy-dihydro-*exo*-dicyclopentadiene having the same index of refraction and density as the product obtained above.

Methoxy-dichloro-dihydro-*exo*-dicyclopentadiene.—Chlorine was bubbled into 196 g. of methoxy-dihydro-*exo*-dicyclopentadiene which was stirred and cooled in an ice-bath. After four hours 72.5 g. of chlorine had been taken up. The product was washed with water and with dilute soda solution and finally, again with water. The oil was dried and distilled *in vacuo*. The fraction boiling at 128–145° (4–5 mm.) amounted to 127 g. Upon refractionation this yielded 111 g. of the purified product boiling at 127–132° (2 mm.). *Anal.* Calcd. for $C_{11}H_{16}Cl_2O$: Cl, 30.2. Found: Cl, 29.8.

Allyloxy-dihydro-*exo*-dicyclopentadiene.—To a stirred mixture of 232 g. of allyl alcohol and 147 g. of dicyclopentadiene there was gradually added 25 g. of boron trifluoride-dibutyl ether $BF_3{\cdot}O(C_4H_9)_2$. The mixture was then heated on a steam-bath under reflux for two hours and then at 110–120° for one hour. The mixture was washed with water, then with dilute sodium hydroxide solution followed by water, and distilled *in vacuo*. The product boiled at 95–105° (5 mm.). The yield was 467 g. or 82%. Upon redistillation it boiled at 117–118° (11 mm.), n^{25}D 1.5000; d^{25}_4 0.9960 (for analysis see Table I).

The *n*-butyl, benzyl and cyclohexyl ethers of hydroxy-dihydro-*exo*-dicyclopentadiene were prepared in the same manner as the allyl ether except that 0.17 mole of $BF_3{\cdot}O(C_2H_5)_2$ was used per mole of dicyclopentadiene. The yields were 60–80%.

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[4] Rivkin and Sheehan, *Ind. Eng. Chem.*, **30**, 1228 (1939).

β-Nitro-isobutyloxy-dihydro-*exo*-dicyclopentadiene.—Boron trifluoride–diethyl ether (40 g.) was added dropwise to a stirred solution of 178.5 g. of 2-nitro-isobutyl alcohol, 198 g. of dicyclopentadiene and 200 cc. of ethylene dichloride at 50°. The temperature was maintained at 50–55° by cooling with ice water. The time required for the addition was thirty minutes. After the exothermic reaction had ceased, the mixture was warmed for six hours at 40–50° then cooled, washed with water and dilute soda solution, followed by a water wash. The product after drying yielded 212 g. of the crude nitro ether as a colorless oil boiling at 160–180° (5 mm.). Upon refractionation this gave 169 g. of the pure product boiling at 136–137° (0.4 mm.).

Phenoxy-dihydro-*exo*-dicyclopentadiene.—To a stirred mixture of 132 g. of dicyclopentadiene and 94 g. of phenol there was added dropwise during the course of thirty minutes 18 g. of 98% sulfuric acid while the reaction mixture was maintained at 28–32° by a cold water-bath. The mixture was stirred thereafter for two hours, then poured into hot water. The oil layer was separated and washed thoroughly with hot water and soda solution. The washed oil was dried, mixed with 1% of its weight of dry sodium carbonate and distilled *in vacuo*. The fraction boiling at 140–150° (1 mm.) was a pale yellow oil. The yield was 98 g. On standing it solidified to a crystalline mass which after recrystallization from methanol with the aid of Norite formed colorless crystals, m. p. 70–71°.

Summary

1. Alcohols and phenols add to dicyclopentadiene in the presence of acidic catalysts (BF_3 or H_2SO_4) to yield rearranged unsaturated ethers, which are derivatives of hydroxy-dihydro-*exo*-dicyclopentadiene.
2. The lower aliphatic ethers thus obtained possess intense floral odors.

PHILADELPHIA, PENN. RECEIVED SEPTEMBER 5, 1945

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, COMMERCIAL SOLVENTS CORPORATION]

Reaction of Primary Aliphatic Amines with Formaldehyde and Nitroparaffins*

BY MURRAY SENKUS

Henry[1,2] has shown that nitromethane reacts with N-hydroxymethyldimethylamine to give 2-nitro-1,3-bisdimethylaminopropane and with N-hydroxymethylpiperidine to give 2-nitro-1,3-bis-(N-piperidyl)-propane; also that N-hydroxymethylpiperidine reacts with nitroethane to give 2-nitro-2-methyl-1,3-bis-(N-piperidyl)-propane and with 3-nitro-1-propanol to give 2-nitro-2-(2-hydroxyethyl)-1,3-bis-(N-piperidyl)-propane. Mousset[3] allowed N-hydroxymethylpiperidine to react with 1-nitro-3-methylbutane and isolated 2-nitro-2-(2-methylpropyl)-1,3-bis-(N-piperidyl)-propane. Duden, Bock and Reid[4] repeated Henry's synthesis of 2-nitro-1,3-bisdimethylaminopropane and reduced the nitro amine with stannous chloride to 2-amino-1,3-bisdimethylaminopropane. They tried to condense N-hydroxymethylamine with nitromethane, but with no success. More recently Cerf[5] made an extensive study of the reaction of nitroparaffins with products derivable from aldehydes and amines and from formaldehyde and amides and on the basis of his work concluded that only 2 moles of a N-hydroxymethyldialkylamine will react with nitromethane and only one mole of a N-hydroxymethyldialkylamine will react with any other primary nitroparaffin. The latter conclusion was in contradiction to Henry's and Mousset's results. Cerf also concluded that N-hydroxymethyldialkylamines do not react with secondary nitroparaffins and that N-hydroxymethylmonoalkylamines do not react with either primary or secondary nitroparaffins.

In spite of the reports mentioned above which indicated that N-hydroxymethylisopropylamine would not react with 2-nitropropane, the reaction was tried. The two compounds reacted smoothly at room temperature to give N-(2-nitroisobutyl)-isopropylamine in 76% conversion. In view of this result the reactions of other N-hydroxymethylmonoalkylamines and other nitroparaffins were investigated and are reported in this paper.

It was also found that N-(2-nitroisobutyl)-isopropylamine can be prepared from 2-nitro-2-methyl-1-propanol and isopropylamine. Presumably the nitro alcohol in the presence of the amine yields 2-nitropropane and formaldehyde. The aldehyde and isopropylamine yield N-hydroxymethylisopropylamine which then reacts with 2-nitropropane as above. Some other nitro amines were prepared from primary amines and nitro alcohols derivable from nitroparaffins and formaldehyde and are reported in this paper.

The nitro amines which were prepared were hydrogenated to the corresponding polyamines. These hydrogenations are also described herein.

Experimental

I. Preparation of Some Nitro Amines from Secondary Nitroparaffins

Two methods were developed for the preparation of nitro amines from secondary nitroparaffins. These methods are described below and the preparation of N-(2-nitroisobutyl)-isopropylamine is used as an example.

Method A. From Isopropylamine, Formaldehyde and 2-Nitropropane.—Two moles of isopropylamine (118 g.) was placed in a two-liter, three-necked flask fitted with a condenser, a sealed stirrer, a dropping funnel and a thermometer reaching into the liquid. The flask was immersed in a water-bath, the temperature of which was maintained at 17–20°. Two moles of 36% (by weight) aqueous formaldehyde was added slowly to the flask while the mixture was agitated. The temperature of the mixture

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* Prepared for the September, 1945, Meeting-in-print.

(1) Henry, *Ber.*, **38**, 2027 (1905).

(2) Henry, *Bull. acad. roy. Belg.*, [3] **33**, 412 (1897).

(3) Mousset, *ibid.*, **622** (1901).

(4) Duden, Bock and Reid, *Ber.*, **38**, 2036 (1905).

(5) Cerf, *Bull. soc. chim.*, [5] **4**, 1451 (1931); [5] **4**, 1460 (1931).