[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Reaction of 1,3-Dienes with Chloral[1]

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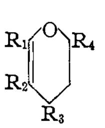
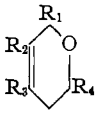
Substituted 5,6-dihydro-1,2-pyrans have been obtained from the reaction of chloral with various 1,3-dienes.

Examples of the formation of substituted 3,4-dihydro-1,2-pyrans (I) from a Diels–Alder type reaction of α,β-unsaturated carbonyl compounds with themselves or with other dienophiles are numerous, a recent example[2] being the formation of bi- and tricyclic dihydropyrans by reaction of α,β-unsaturated carbonyl compounds with vinyl ethers. However, reports of the formation of substituted 5,6-dihydro-1,2-pyrans (II) by direct condensation of 1,3-dienes with aldehydes are few. Gresham and Steadman[3] obtained a 61% yield of 2,4-dimethyl-5,6-dihydro-1,2-pyran (II, $R_1, R_3 = CH_3$; $R_2, R_4 = H$) by heating 1,3-dimethylbutadiene with formaldehyde in a sealed vessel. Although these workers were unable to show that butadiene or piperylene would react with formaldehyde under similar conditions, small amounts of 5,6-dihydro-1,2-pyran have been observed among the products resulting from the acid-catalyzed condensation of butadiene with formaldehyde.[4–7]



I



II

In this research, chloral has reacted with various 1,3-dienes in sealed tubes at 150° for periods of 24 hours. As expected, the enhanced positive character of the carbonyl group promoted the Diels–Alder type of reaction. The results are shown in Table I and derivatives of the primary adducts are given in Table II.

The unsymmetrical dienes, isoprene and piperylene, could lead to a mixture of isomers but in these experiments only single products were obtained. The product from the condensation of piperylene and chloral was assigned the structure 2-methyl-6-trichloromethyl-5,6-dihydro-1,2-pyran and that from the condensation of isoprene and chloral the structure 4-methyl-6-trichloromethyl-5,6-dihydro-1,2-pyran. These assignments of structure were made on the basis of polarizations in the diene due to hyperconjugation. The same reasoning was employed by Gresham and Steadman in assigning a structure to the adduct from formaldehyde and 1,3-dimethylbutadiene and proved correct by oxidation of the hydrogenated adduct to unique fragments.

Although Gresham and Steadman observed no condensation to occur between formaldehyde and piperylene in the absence of catalysts, in the present study acetaldehyde was caused to react with isoprene in 4% yield. A condensation could not be effected between chloral and butadiene and the attempted reactions also failed between chloral and 1,4-diphenylbutadiene or styrene.

Of the other carbonyl compounds investigated, bromal was too reactive to give any definite products with 2,3-dimethylbutadiene, isoprene or butadiene. Vigorous and extensive decomposition occurred with evolution of hydrogen bromide even at initially moderate temperatures. Nor could any reaction be effected between 2,3-dimethylbutadiene and ethylene oxide or acetyl chloride at a temperature of 180° in a period of 24 hours. Dimethylformamide could not be induced to react with 2,3-dimethylbutadiene even at 170° in a period of 24 hours. This observation demonstrates the effect of a neighboring electron-releasing group. Attempts to condense benzaldehyde, anisaldehyde, *p*-chlorobenzaldehyde and *p*-nitrobenzaldehyde with isoprene or 2,3-dimethylbutadiene were not successful when the combined reagents were heated at 150° for 24 hours.

Experimental

All melting points were taken with the Fisher–Johns apparatus.

Condensation of Chloral with 2,3-Dimethylbutadiene. 3,4-Dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran.—Into a carius tube was placed 32 ml. (0.33 mole) of chloral, 37 ml. (0.33 mole) of 2,3-dimethylbutadiene and a few milligrams of hydroquinone. The sealed tube was placed in a 150° oven for a period of 24 hours. The cooled tube was then opened and the red-brown liquid was fractionated in a 125-ml. modified Claisen flask, packed with glass helices. There was obtained 40.3 g. (53%) of colorless liquid, b.p. 99–100° (4.5 mm.), n^{25}_{D} 1.5060, d^{25} 1.3010.

Anal. Calcd. for $C_8H_{11}OCl_3$: C, 41.86; H, 4.83. Found: C, 41.91; H, 5.10. Calcd. for $C_8H_{11}OCl_3$: mol. ref., 52.70; mol. wt., 230; one double bond. Found: mol. ref., 52.52; mol. wt. (Rast) 226; number of double bonds, 1.02 (hydrogenation).

Addition of Bromine to 3,4-Dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran. 3,4-Dibromo-3,4-dimethyl-6-trichlorotetrahydropyran.—Five grams (0.0218 mole) of 3,4-dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran, dissolved in 50 ml. of carbon tetrachloride, was cooled in a Dry Ice–acetone-bath. Bromine was added dropwise until a slight red color persisted. The solution was then allowed to warm to room temperature and the solvent was removed under reduced pressure. A viscous oil remained which was dissolved in hot ethanol and the resulting solution was cooled in a Dry Ice–acetone-bath. Fine, colorless needles were obtained which were recrystallized from ethanol; yield 7.78 g. (92%), m.p. 112.5–113°.

Anal. Calcd. for $C_8H_{11}OBr_2Cl_3$: C, 24.67; H, 2.85. Found: C, 24.72; H, 2.92.

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(1) Taken from a thesis submitted by A. J. S. to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the M.A. degree.

(2) W. S. Emerson, G. H. Birum and R. I. Longley, THIS JOURNAL, **75**, 1312 (1953).

(3) T. L. Gresham and T. R. Steadman, *ibid.*, **71**, 737 (1949).

(4) W. F. Gresham and W. E. Grigsby, U. S. Patent 2,493,964 (1950).

(5) O. C. Dermer, L. Kohn and W. J. Nelson, THIS JOURNAL, **73**, 5869 (1951).

(6) Badische Anilin- und Sodafabrik (Friedrichsen, inventor), German Patent 800,298 (1950); *C.A.*, **45**, 1628f (1951).

(7) S. Olsen, E. Hidle, G. Svenneby and E. Finsnes, *Acta Chem. Scand.*, **6**, 859 (1952).

TABLE I

PRIMARY PRODUCTS

Adduct	B.p., °C.	Mm.	Yield, %	n^{25}D	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,3-Dimethylbutadiene + chloral	99–100	4.5	53	1.5060	$C_8H_{11}OCl_3$	41.86	41.91	4.83	5.10
Isoprene + chloral	83–85	1	30	1.5050	$C_7H_9OCl_3$	39.01	39.05	4.21	4.61
Piperylene + chloral	70–71	5	32	1.4940	$C_7H_9OCl_3$	39.01	38.93	4.21	4.48
Isoprene + acetaldehyde	115–116		4	1.4601	$C_7H_{12}O$	74.95	75.04	10.78	10.62

TABLE II

DERIVATIVES OF PRIMARY ADDUCTS

Adduct, derivatives		B.p. or (m.p.) °C.	Mm.	Yield, %	n^{25}D	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,3-Dimethylbutadiene + chloral										
Dibromide	M.p.	112.5–113		92		$C_8H_{11}OBr_2Cl_3$	24.67	24.72	2.85	2.92
Tetrahydropyran	B.p.	88–90	5	96	1.4878	$C_8H_{13}OCl_3$	41.49	41.75	5.66	5.76
Isoprene + chloral										
Dibromide	M.p.	72–73		97		$C_7H_9OBr_2Cl_3$	22.40	22.48	2.42	2.57
Tetrahydropyran	B.p.	65–66.5	5	97	1.4913	$C_7H_{11}OCl_3$	38.65	38.40	5.10	5.40
Piperylene + chloral										
Dibromide	M.p.	79–79.5		95		$C_7H_9OBr_2Cl_3$	22.40	22.27	2.42	2.36
Tetrahydropyran	B.p.	75–76	4	94	1.4831	$C_7H_{11}OCl_3$	38.65	38.56	5.10	5.45

Hydrogenation of 3,4-Dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran. 3,4-Dimethyl-6-trichloromethyltetrahydropyran.—Into a thick-walled hydrogenation bottle was placed 8.00 g. (0.035 mole) of 3,4-dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran, 30 ml. of 95% ethanol and a few milligrams of platinum oxide. Hydrogenation was complete in one-half hour under a pressure of 50 pounds. After removal of the solvent, a viscous oil remained which was distilled at 88–90° (5 mm.), n^{25}D 1.4878; yield 7.76 g. (96%).

Anal. Calcd. for $C_8H_{13}OCl_3$: C, 41.49; H, 5.66. Found: C, 41.75; H, 5.76.

Attempted Hydrolysis of 3,4-Dimethyl-6-trichloromethyl-5,6-dihydro-1,2-pyran.—Several attempts to hydrolyze the trichloromethyl group using basic catalysts were unsuccessful. The starting material was recovered almost completely. In one experiment, using sodium hydroxide, diethylene glycol and water, only 20% of the starting material was recovered, but no pure product could be isolated from the reaction mixture.

Condensation of Chloral with Isoprene. 4-Methyl-6-trichloromethyl-5,6-dihydro-1,2-pyran.—Into a carius tube was placed 33 ml. (0.33 mole) of isoprene, 32 ml. (0.33 mole) of chloral and a few milligrams of hydroquinone. The sealed tube was heated for 24 hours in a 150° oven. The tube was then cooled, opened and its contents were fractionated in a modified Claisen flask. There was obtained 21.6 g. (30%) of colorless liquid, b.p. 83–85° (1 mm.), n^{25}D 1.5050, number of double bonds, 1.08 (hydrogenation).

Anal. Calcd. for $C_7H_9OCl_3$: C, 39.01; H, 4.21. Found: C, 39.05; H, 4.61.

Addition of Bromine to the Chloral–Isoprene Adduct. 3,4-Dibromo-4-methyl-6-trichloromethyltetrahydropyran.—The addition of bromine was carried out as described above. From 5.0 g. (0.023 mole) of adduct was obtained 8.5 g. (97%) of white crystalline solid which was recrystallized from ethanol; m.p. 72–73°.

Anal. Calcd. for $C_7H_9OBr_2Cl_3$: C, 22.40; H, 2.42. Found: C, 22.48; H, 2.57.

Hydrogenation of the Chloral–Isoprene Adduct. 4-Methyl-2-trichloromethyltetrahydropyran.—The hydrogenation of the chloral–isoprene adduct was carried out as described previously. From 10.0 g. (0.0465 mole) of adduct was obtained 10.4 g. (97%) of the tetrahydropyran, b.p. 65–66.5° (5 mm.), n^{25}D 1.4913.

Anal. Calcd. for $C_7H_{11}OCl_3$: C, 38.65; H, 5.10. Found: C, 38.40; H, 5.40.

Condensation of Chloral with Piperylene. 2-Methyl-6-trichloromethyl-5,6-dihydro-1,2-pyran.—Thirty-two milliliters (0.33 mole) of piperylene, 32 ml. (0.33 mole) of chloral and a few milligrams of hydroquinone were sealed in a carius tube and then heated in a 150° oven for 24 hours. The reaction product was fractionated as described previously. The yield was 22.5 g. (32%) of colorless liquid, b.p. 70–71° (5 mm.), n^{25}D 1.4940, number of double bonds, 1.05 (hydrogenation).

Anal. Calcd. for $C_7H_9OCl_3$: C, 39.01; H, 4.21. Found: C, 38.93; H, 4.48.

Addition of Bromine to the Chloral–Piperylene Adduct. 3,4-Dibromo-2-methyl-6-trichloromethyltetrahydropyran.—The addition of bromine to the chloral–piperylene adduct was carried out as described previously. From 5.0 g. (0.0232 mole) of adduct there was obtained 8.3 g. (95%) of white solid which, after recrystallization from ethanol, melted at 79–79.5°.

Anal. Calcd. for $C_7H_9OBr_2Cl_3$: C, 22.40; H, 2.42. Found: C, 22.27; H, 2.36.

Hydrogenation of the Chloral–Piperylene Adduct. 2-Methyl-6-trichloromethyltetrahydropyran.—The hydrogenation of the chloral–piperylene was performed as described above. From 5.0 g. (0.023 mole) of adduct was obtained 4.7 g. (94%) of colorless liquid, b.p. 75–76° (4 mm.), n^{25}D 1.4831.

Anal. Calcd. for $C_7H_{11}OCl_3$: C, 38.65; H, 5.10. Found: C, 38.56; H, 5.45.

Condensation of Acetaldehyde with Isoprene. 4,6-Dimethyl-5,6-dihydro-1,2-pyran.—Into a carius tube were placed 33 ml. (0.33 mole) of isoprene, 21 ml. (0.33 mole) of acetaldehyde and a few milligrams of hydroquinone. The sealed tube was placed in a 150° oven for 24 hours. The contents of the tube were fractionated at atmospheric pressure. Fifteen milliliters of isoprene was recovered but there was obtained 3 g. of colorless material which distilled at 113–117°. The crude product was washed with 10% sodium bicarbonate solution and dried over calcium chloride. Distillation yielded 1.5 g. (4%) of 4,6-dimethyl-5,6-dihydro-1,2-pyran, b.p. 115–116°, n^{25}D 1.4601. The compound added bromine in carbon tetrachloride and gave negative tests for the aldehyde group.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.04; H, 10.62.

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