The Chemistry of α,β-Unsaturated Ethers. V. Diels-Alder Reaction of Paraformaldehyde and 1-Alkoxy-1,3-alkadienes[1]

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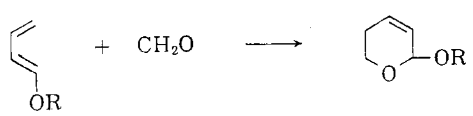
Gresham and Steadman[3] reported the first instance of a carbonyl group (formaldehyde) acting as a dienophile. The reaction was successful for 2-methyl-1,3-pentadiene with paraformaldehyde yielding 2,4-dimethyl-5,6-dihydro-2*H*-pyran but was unsuccessful with 1,3-butadiene or piperylene. Dale and Sisti[4] have shown that chloral will act as a dienophile with certain dienes including 2,3-dimethylbutadiene, isoprene, and piperylene to yield 5,6-dihydro-2*H*-pyrans. Acetaldehyde and isoprene gave a low yield of a dihydropyran but a number of other carbonyl containing compounds were unreactive with isoprene or 2,3-dimethylbutadiene.

We have found that an alkoxy group on the 1-position of a 1,3-alkadiene provides sufficient activation to permit the Diels-Alder reaction with paraformaldehyde. The reaction products are 2-alkoxy-5,6-dihydro-2*H*-pyrans.



In addition to the combination of 1-ethoxy-1,3-butadiene and paraformaldehyde, we have used five other 1-alkoxydienes with paraformaldehyde. The dienes used and the results obtained are shown in Table I. The physical properties and analyses of the products are shown in Table II.

We were not able to obtain a reaction with 1-methoxy-1,3-butadiene with either 40% formalin or metaformaldehyde. Other reactant combinations which were unsuccessful include 1-ethoxy-4-methyl-1,3-octadiene with paraformaldehyde and 1-acetoxy-1,3-butadiene with paraformaldehyde. Several experiments were made with chloral and 1-methoxy-1,3-butadiene, each of which resulted in extensive charring of the mixture and the evolution of copious quantities of hydrogen chloride.

From our results we would anticipate that dienes with electron-attracting groups would fail in this reaction but that dienes with electron donating groups, such as the dimethylamino group,[5] would react with paraformaldehyde.

It has not been established for this type of reactions if they are acid-catalyzed and thus a variation of the Prins reaction, or if they are a thermal process and thus a Diels-Alder reaction. The paraformaldehyde of our work contained, at the most, a trace of acid (less than 0.01% calcd. as formic acid). Inasmuch as paraformaldehyde is made by an acid-catalyzed process, it is possible that there is present a trace of mineral acid and this trace may be all that is required to promote the reaction with active dienes. There have been many studies made on the acid-catalyzed process including dienes and alkenes with formaldehyde.[6] We are not prepared to say which type of reaction is involved in our work but we have classified it as a Diels-Alder reaction on the basis that there was a trace of acid present, at the most.

The product from the reaction of 1-ethoxy-1,3-butadiene and paraformaldehyde was shown to be the known 2-ethoxy-5,6-dihydro-2*H*-pyran by its 2,4-dinitrophenylhydrazone and by its conversions to 2-ethoxytetrahydropyran and to 2,4-pentadienal.[7]

The structures for the adducts of the other 1-alkoxy-1,3-butadienes and paraformaldehyde were assigned as the 2-alkoxy-5,6-dihydro-2*H*-pyrans on the basis of elemental analyses and that they each yielded the same 2,4-dinitrophenylhydrazone as was obtained from 2-ethoxy-5,6-dihydro-2*H*-pyran. The products from the reactions of 1-methoxy-1,3-hexadiene and of 1-methoxy-2-ethyl-1,3-butadiene with paraformaldehyde are assumed to have this same pyran structure inasmuch as they are both unsaturated and readily form 2,4-dinitrophenylhydrazones.

EXPERIMENTAL[8]

The 1-alkoxy-1,3-alkadienes were prepared from the 1,1,3-trialkoxyalkanes as previously described.[1] The paraformaldehyde was Mallinckrodt's "Photo-Purified" grade and contained less than 0.01% acid calculated as formic acid.

2-Ethoxy-5,6-dihydro-2H-pyran. A mixture consisting of 588 g. (6.0 moles) of 1-ethoxy-1,3-butadiene, 180 g. (6.0 moles) of paraformaldehyde and 2 g. of hydroquinone was heated in a rocker bomber for 6 hr. at 180°. The mixture was distilled under reduced pressure to recover 430 g. (56%) of 2-ethoxy-5,6-dihydro-2*H*-pyran boiling at 51-54° (20 mm.). The product was washed with water to remove the last traces of paraformaldehyde and redistilled to provide a sharp boiling fraction at 53-54° (20 mm.); n_{D}^{20} 1.4432 (analysis given in Table II).

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(1) Paper IV. D. G. Kubler, *J. Org. Chem.*, **27**, 791 (1962).

(2) Furman University, Greenville, S. C.

(3) T. L. Gresham and T. R. Steadman, *J. Am. Chem. Soc.*, **71**, 737 (1949).

(4) W. J. Dale and A. J. Sisti, *J. Am. Chem. Soc.*, **76**, 81 (1954).

(5) M. F. Fegley, N. M. Bortnick, and C. H. McKeever, *J. Am. Chem. Soc.*, **79**, 4140 (1957).

(6) See ref. 4 for some of these studies and for more recent work on the reactions of alkenes with paraformaldehyde see A. T. Blomquist and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 6025 (1957) and references cited there.

(7) G. F. Woods and H. Sanders, *J. Am. Chem. Soc.*, **68**, 2483 (1946).

(8) We wish to thank Mr. W. H. Rankin for assistance with much of the experimental work and Mr. J. Bodenschatz for the elemental analyses. All melting points are corrected and the boiling points are uncorrected.

TABLE I

REACTION OF 1-ALKOXY-1,3-ALKADIENES AND PARAFORMALDEHYDE

Dienes, Moles	Paraformaldehyde, Moles	Product 5,6-Dihydro-2*H*-pyran	Yield, %
1-Ethoxy-1,3-butadiene, 6.0[a]	6.0	2-Ethoxy, I	56
1-Methoxy-1,3-butadiene, 6.0[b]	6.0	2-Methoxy, II	62
1-(2-Methoxyethoxy)-1,3-butadiene, 1.5[b]	1.5	2-(2-Methoxyethoxy), III	30
1-(2-Ethylhexoxy)-1,3-butadiene, 0.18[b]	0.18	2-(2-Ethylhexoxy), IV	32
1-Methoxy-1,3-hexadiene, 4.4[c]	4.0	2-Methoxy-5-ethyl, V	21
1-Methoxy-2-ethyl-1,3-butadiene, 0.87[b]	0.92	2-Methoxy-3-ethyl, VI	29

[a] See the Experimental section for the general procedure which is described for this reactant combination. [b] This mixture was heated for 4 hours at 180° in an autoclave. DuPont "Antioxidant No. 5" (*p*-*N*-butylaminophenol in a mixed solvent of methanol and 2-propanol) was used as a polymerization inhibitor. [c] Pyrogallol (2 g.) was used as a polymerization inhibitor.

TABLE II

PROPERTIES AND ANALYSES OF PRODUCTS

			Carbon, %		Hydrogen, %		Unsaturation, %[a]		2,4-Dinitrophenylhydrazone[b]		
										Nitrogen, %	
Product	B.P., (mm.)	n^{20}_{D}	Calcd.	Found	Calcd.	Found	Calcd.	Found	M.P.	Calcd.	Found
I	53–54 (20)	1.4432	65.59	65.34	9.44	9.87	15.60	15.43	168–169.5[c]	20.00	19.88
II	59–60 (50)[d]	1.4452	63.13	63.10	8.84	9.20	17.50	17.25	168–169[c]	—	—
III	74–75 (5)	1.4531	60.74	60.90	8.92	9.00	12.64	12.62	165–167[c]	—	—
IV	93–94 (2)	1.4530	73.54	73.00	11.39	11.40	9.42	9.33	166–168[c]	—	—
V	69–70 (20)	1.4466	67.57	67.42	9.93	10.00	14.06	14.00	131–132	18.17	18.56
VI	67–69 (20)	1.4506	67.57	66.60	9.93	9.90	14.06	13.78	141–142	18.17	18.14

[a] Determined by bromination. [b] Prepared as described in the Experimental section. [c] Mixture melting point determinations showed no depression of melting points. [d] Other properties we have measured are: b.p. 136–138° (760 mm.); sp. gr. $^{20°}_{20°}$ 1.008; n^{25}_{D} 1.4425.

The 2,4-dinitrophenylhydrazone was made by adding the pyran to the standard reagent[9] and warming the mixture on a steam bath. The bright yellow plates (from ethanol–water) turned red at about 125° and then melted at 168–169.5° (analysis given in Table II).

The literature values for 2-ethoxy-5,6-dihydro-2*H*-pyran are[7]: b.p. 153–155°; n^{25}_{D} 1.4475; 2,4-dinitrophenylhydrazone, m.p. 159–160°. Because of the discrepancies of these values and of ours, we obtained an authentic sample of the pyran[10] and prepared the 2,4-dinitrophenylhydrazone under the same conditions we had used for our material. The derivative was identical to ours in appearance, melting point, and mixture melting point. Inasmuch as the 2,4-dinitrophenylhydrazone obtained by Woods and Sanders was prepared by hydrolyzing the pyran with aqueous acid to 5-hydroxy-2-pentenal and then adding the reagent, it is possible that the two materials are *cis-trans* isomers, ours being the *cis* and theirs the *trans*. To be sure that dehydration or other chemical changes had not occurred by the conversion of the yellow plates to the red plates we heated a sample at 142° in a drying pistol (under vacuum) for 3 hr.

Anal. Calcd. for $C_{11}H_{12}N_4O_5$: N, 20.00. Found: N, 19.75.

2-Ethoxytetrahydropyran. The 2-ethoxy-5,6-dihydro-2*H*-pyran (344 g., 2.68 moles) was hydrogenated over Raney nickel in a stirred autoclave. The 299 g. (86%) of 2-ethoxytetrahydropyran distilled at 46–47° (20 mm.); n^{20}_{D} 1.4247. The 2,4-dinitrophenylhydrazone melted at 106.5–107°. The corresponding values for an authentic sample of 2-ethoxytetrahydropyran[11] were: b.p. 46–47 (20 mm.), n^{20}_{D} 1.4250 and the 2,4-dinitrophenylhydrazone melted at 107–108°. The infrared spectra of the 2-ethoxytetrahydropyran from the two sources were identical.

2,4-Pentadienal. This material was prepared by the procedure essentially like that of Woods and Sanders.[7] A mixture of 128 g. (1.0 mole) of 2-ethoxy-5,6-dihydro-2*H*-pyran, 80 ml. of 85% phosphoric acid, and 200 ml. of water was stirred at room temperature for 30 min. The resulting homogeneous solution was steam distilled. The organic layer was dried and distilled to yield 20 g. (24%) of 2,4-pentadienal boiling at 37° (20 mm.); n^{20}_{D} 1.5173; and 2,4-dinitrophenylhydrazone of m.p. 173–174°. The reported values[7] for this material are: b.p. 37–38° (20 mm.); n^{20}_{D} 1.5163; and 2,4-dinitrophenylhydrazone of m.p. 176–177°.

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[9] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, 1956.

[10] We wish to thank Dr. G. F. Woods of the University of Maryland for this sample.

[11] Prepared as described by R. I. Longley, W. S. Emerson, and T. C. Shafer, *J. Am. Chem. Soc.*, **74**, 2012 (1952).

Two Stable α-Carbethoxy Ketenes[1]

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In the course of a synthetic scheme an attempt was made to convert α-carbethoxy-β-phenylisovaleric acid (I) to α-carbethoxy-β-phenylisovaleroyl chloride (II) by reaction with thionyl chloride.

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