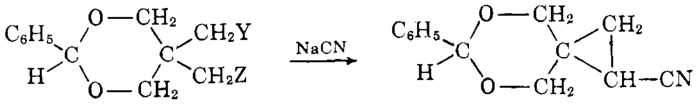
Table IV

Displacement Reactions of *O*-Benzylidenepentaerythritol Derivatives with Sodium Cyanide



Experiment no.	Substrate		Yield,[a] %	Solvent
	Y	Z		
1	$OSO_2C_6H_5$	$OSO_2C_6H_5$	45	DMF
2	$OSO_2C_6H_5$	I	77	DMF
3	I	I	45	DMF
4	$OSO_2C_6H_5$	I	36	DMSO[b]
5	$OSO_2C_6H_5$	I	31	Anhydrous DMSO,[b] solid NaCN introduced
6	$OSO_2C_6H_5$	I	30	Anhydrous DMF, solid NaCN introduced
7	$OSO_2C_6H_4Br(p)$	$OSO_2C_6H_4Br(p)$	85	DMF
8	$OSO_2C_6H_4Br(p)$	I	82	DMF
9	$OSO_2C_6H_4CH_3(p)$	$OSO_2C_6H_4CH_3(p)$	7.5[c]	DMF
10	$OSO_2C_6H_4CH_3(p)$	I	34	DMF
11	$OSO_2C_6H_5$	$OSO_2C_6H_5$	Very low	C_2H_5OH[d]

[a] Yields based upon materials with melting points within 2° or less of the analytical samples. [b] Reaction at 130–135°. [c] 38% substrate recovered. [d] Reaction carried out in a Carius bomb tube at 130° for 8 hr.

6.26 p.p.m., assignable to the methylene hydrogens of the lactone ring and the chloromethyl group, respectively. The upfield peaks were located at $\tau = 7.93$, 8.53, and 8.86 p.p.m. for the three nonequivalent cyclopropane ring hydrogens. The approximate peak areas were 2, 2, 1, 1, and 1 for the different types of hydrogens in the order described.

Acknowledgment.—We are grateful to the Strasenburgh Laboratories for support of a portion of this investigation and thank Robert C. Hirst for the nuclear magnetic resonance spectral data and interpretation.

Synthesis of 1,5,9-Cyclododecatriene

Hirosi Takahasi and Muneaki Yamaguchi

Government Industrial Research Institute, Osaka, Japan

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Cyclic dimers[1] and trimers[2] of butadiene have been obtained by several workers. We have now found that a trimer, *trans,trans,cis*-1,5,9-cyclododecatriene, is produced upon treatment of butadiene with a novel catalyst system which consists of a combination of an alkylaluminum halide and a titanium tetraalkoxide. The action of trialkylaluminum–titanium tetraalkoxide complex on butadiene has been reported by Wilke[3] to afford 1,2-polymer.

A benzene solution of diethylaluminum chloride containing titanium tetrabutoxide in a mole ratio of about 20 (Al/Ti) was treated with butadiene gas until the absorption rate decreased rapidly. Distillation of the reaction products gave a cyclododecatriene fraction in 81% yield, no appreciable quantities of dimer and tetramer being isolated. The cyclododecatriene consisted only of *trans,trans,cis*-1,5,9-cyclododecatriene and no *trans,trans,trans* isomer was isolated upon careful distillation in any case. However, the *all trans* isomer was isolated in about 5% yield from trimerization products of butadiene in the presence of a mixture of titanium tetrachloride and dialkylaluminum halide, as reported by Wilke. Consequently, it appears that our catalysts containing titanium tetraalkoxides have higher stereospecificity for trimerization of butadiene than catalysts reported by Wilke.

trans,trans,cis-1,5,9-Cyclododecatriene has been identified by measurements of molecular weight and infrared spectrum and by formation of silver nitrate complex in quantitive yield.[4] Catalytic hydrogenation and ozonization yielded cyclododecane and succinic acid, respectively, in high yeilds.

Effects of reaction variables on yields of cyclododecatriene have been examined. As summarized in Table I, the organic groups of titanium tetraalkoxides and organoaluminum compounds had minor effects on the yields of cyclododecatriene. Alkylaluminum bromides and chlorides were equally active. The halogen content of organoaluminum compounds or n in $R_{3-n}AlX_n$ must be between 0.5 and 1.5. When n was 0.5 or less, linear polymer was produced in quantities and cyclododecatriene was obtained with poor yields or in trace. Similar results were also observed when n was 1.5 or more.

Data in Table II show that the mole ratio of alkylaluminum halides to titanium tetraalkoxides must be greater than 12. When the mole ratio was less than 12, little, if any, butadiene was absorbed and polymer was produced instead of cyclododecatriene. At a mole ratio of 18 or higher, the absorption rate of butadiene was increased appreciably and yields of cyclododecatriene were greatly improved. The yields remained approximately constant at higher mole ratios. In each case certain induction period was recognized.

As shown in Table III, the reaction temperature should be kept below 65°. Higher temperatures than

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(1) (a) K. Ziegler, *Angew. Chem.*, **59**, 177 (1947); H. W. B. Reed, *J. Chem. Soc.*, 685 (1951); (b) G. Wilke, *Angew. Chem.*, **73**, 33 (1961).

(2) (a) G. Wilke, *ibid.*, **69**, 397 (1957); Studiengesellschaft Kohle m. b. H., Belg. Patent 555,180 (1957); G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); (b) Studiengesellschaft Kohle m. b. H., Belg. Patent 566,436 (1958); G. Wilke and H. Müller, German Patent 1,043,329 (1958); (c) *cf.* also ref. 1b.

(3) G. Wilke, *Angew. Chem.*, **68**, 306 (1956).

(4) Compared with a silver nitrate complex of *trans,trans,cis*-1,5,9-cyclododecatriene obtained by method of Wilke.

TABLE I

THE EFFECT OF CATALYSTS

Ti(OR)$_4$		$R_{3-n}AlX_n$					Time, hr.	Temp., °C.	$C_{12}H_{18}$[b]	
R	g.	R	X	n	g.	Al/Ti[a]			g.	%
C_4H_9	0.5	C_2H_5	Br	1	5	20.6	3	30–35	33	85
C_4H_9	0.5	CH_3	Cl	1	2.6	19	2	30–35	2	33
C_4H_9	0.5	CH_3	Cl	1	5.2	38	2	30–35	7	70
C_4H_9	1.3	CH_3	Cl	1	7.4	20.8	2	62	10	42
C_4H_9	0.36	CH_3	Cl	1.5	2.2	20	3	30–35	Trace	
C_4H_9	0.48	CH_3	Cl	1.5	5.7	40	3	30–35	0.5	7
C_4H_9	0.34	C_2H_5	Cl	0.5	1.1	10	2	40	0[c]	
C_4H_9	0.34	C_2H_5	Cl	0.5	2.1	20	2	40	3	35
C_4H_9	0.34	C_2H_5	Cl	0.5	3.3	30	2	40	2	27
C_6H_5	0.8	C_2H_5	..	0	2					
		CH_3	Cl	1.5	2[d]	21	2	30–35	11	73

[a] Mole ratio of $R_{3-n}AlX_n/Ti(OR)_4$. [b] Cyclododecatriene, b.p. 85–95° at 5 mm. [c] No absorption of butadiene was observed but a trace of linear polymer was obtained. [d] To a benzene solution of titanium tetraphenoxide was added triethylaluminum and then methylaluminum sesquichloride.

TABLE II

THE EFFECT OF Al/Ti MOLE RATIO[a]

$Ti(OC_4H_9)_4$ g.	$(C_2H_5)_{3-n}AlCl_n$			Time, min.	Temp., °C.	C_4H_6[c] l.	$C_{12}H_{18}$[d]	
	n	g.	Al/Ti[b]				g.	%
1	1.24	4.2	12.0	120	40–50	8	2	10
0.6	1.24	2.8	13.4	180	40–50	17	21	54
1	1.24	6	17.2	120	40–50	6.9	14	85
0.17	1.27	0.96	15.7	50	31	1.2	Trace	
0.17	1.27	1.2	20.0	121	31	13.4	28.1	86.7
0.17	1.27	1.2	20.0	41	45	6.8	14.6	89
0.085	1.27	0.78	24.0	36	45	5.4	11.7	90
0.17	1.27	1.0	24.6	57	31	2.6	5.0	79
0.17	1.27	1.8	29.4	110	28	4.5	8.1	75
0.17	1.27	3.0	49.2	95	31	5.1	10.0	80

[a] The reactions were carried out in 40 ml. of benzene. [b] Mole ratio of $(C_2H_5)_{3-n}AlCl_n/Ti(OC_4H_9)_4$ [c] Absorbed butadiene. [d] Cyclododecatriene, b.p. 85–95° at 5 mm.

TABLE III

THE EFFECT OF TEMPERATURE[a]

$Ti(OC_4H_9)_4$ g.	$(C_2H_5)_{3-n}AlCl_n$			Temp. °C.	Time, min.	$C_{12}H_{18}$[c]	
	n	g.	Al/Ti[b]			g.	%
1.0	1.24	6.5	18	30–35	60	14	81
1.0	1.24	6.5	18	64	60	9	30
0.034	1.73	0.47	39	30	65	1.0	55
0.034	1.73	0.47	39	45	77	4.5	82
0.034	1.73	0.47	39	59	85	9.2	83
0.034	1.73	0.47	39	72	50	0.8	72

[a] The reactions were carried out in 40 ml. of benzene. [b] Mole ratio of $(C_2H_5)_{3-n}AlCl_n/Ti(OC_4H_9)_4$. [c] Cyclododecatriene, b.p. 85–95° at 5 mm.

65° during preparation of catalyst or reaction resulted in nearly complete loss of catalyst activity and negligible yields of cyclododecatriene.

After butadiene was passed for eight hours into a benzene solution of diethylaluminum chloride and titanium tetrabutoxide in a mole ratio of 22, the absorption slowed down rapidly. Addition of diethylaluminum chloride to the reaction mixture regenerated the activity of the catalyst system allowing the reaction proceeding for an additional several hours. Cyclododecatriene was obtained in about 80% yield from this reaction mixture and the production of linear polymer was not appreciably increased.

Experimental[5]

Synthesis of *trans,trans,cis*-1,5,9-Cyclododecatriene.—To a solution of 1.7 g. of titanium tetrabutoxide in 50 ml. of benzene, 13 g. of diethylaluminum chloride was added in a nitrogen atmosphere, with stirring while the temperature was maintained below 55°. Immediately gas was evolved and the solution became brown-black. To the catalyst solution thus obtained and held at 50–55°, butadiene was introduced through calcium chloride tube at such a rate that most of the added butadiene was consumed. The absorption rate was about 4 l. per 10 min. for a period of 8 hr. but after that it decreased rapidly. The total volume of butadiene absorbed was 165 l. After standing overnight, the reaction mixture was treated with alcohol and dilute hydrochloric acid, and organic layer was combined with benzene extracts of water layer and distilled to afford a fraction (320 g. or 81%) boiling at 85–95° (5 mm.) and residue (70 g.). The fraction was redistilled with a high-efficiency rotating band column, to afford *trans,trans,-cis*-1,5,9-cyclododecatriene boiling at 96° (10 mm.) in more than 95% recovery. Though the forerun of the redistillation was cooled at −20° for several days, no crystalline *trans,trans,trans* isomer was obtained. Infrared spectrum of the forerun agreed with that of *trans,trans,cis* isomer.

The molecular weight of *trans,trans,cis*-1,5,9-cyclododecatriene was determined by mass spectrometric analysis as 162; n^{25}_D 1.5051, d^{25}_4 0.8895. The silver nitrate complex melted at 166–167°[6]. Mixtures of the complex with authentic sample

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(5) All temperatures are uncorrected.

(6) D. N. Saxarkin and B. B. Korneba, *Dokl. Akad. Nauk, SSSR*, **132**, 1078 (1960).

melted at 166–167°. Infrared absorptions (liquid film) of *trans* and *cis* double bonds were observed at 970 and 705 cm.$^{-1}$, respectively, and the *trans* absorption was stronger than *cis*. Catalytic hydrogenation over palladium–charcoal yielded cyclododecane melting at 58–59°[7] in 91% yield.

Synthesis of Cyclododecatrienes by Method of Wilke.[8]—A mixture of 9 g. of diethylaluminum bromide and 1.7 g. of titanium tetrachloride was treated with butadiene at about 50° for 6 hr. A cyclododecatriene fraction (60 g.) was obtained in 80% yield. The fraction consisted largely of *trans,trans,cis*-1,5,9-cyclododecatriene boiling at 96° (10 mm.) and about 5% of *trans,trans,trans* isomer boiling at 92° (10 mm.), which was separated as a forerun on distillation through a high-efficiency rotating band column. The *trans,trans,trans* isomer fraction crystallized on cooling and the solid melted at 31–32°.[9]

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(7) M.p. 60°, L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenogen, *Helv. Chim. Acta*, **13**, 1152 (1930).

(8) See also ref. 2a.

(9) G. Wilke and M. Kröner, *Angew. Chem.*, **71**, 574 (1959), reported m.p. 33–34°.

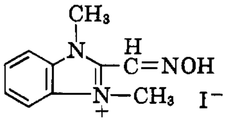
Methylation of Benzimidazole and Benzothiazole Carboxaldoximes[1]

E. J. Poziomek,[2] R. H. Poirier,[3] R. D. Morin,[3] and
T. F. Page, Jr.[3]

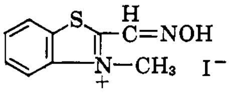
U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Maryland, and Battelle Memorial Institute, Columbus, Ohio

Received April 30, 1962

In the course of our studies on quaternary heterocyclic aldoxime salts, we had occasion to prepare 1,3-dimethyl-2-formylbenzimidazolium iodide oxime (I) and 2-formyl-3-methylbenzothiazolium iodide oxime (II) through schemes involving methylation of 1-methylbenzimidazole-2-carboxaldoxime and benzothiazole-2-carboxaldoxime, respectively. The usual synthesis of quaternary heterocyclic aldoximes involves alkylation of the appropriate heterocyclic aldoximes in acetone or alcohol.[4] With oximes that are difficult to alkylate it has been reported that nitromethane is a better choice of solvent.[5] When the ring nitrogen is hindered sterically, alkylation is very difficult and in the case of quinoline-2-aldoxime it was unsuccessful.[4a] In the case where a methyl group at the 6-position of picolinaldehyde oxime hinders the ring nitrogen sterically, it was shown that alkylation occurs on the nitrogen of the oxime rather than on the ring.[6]



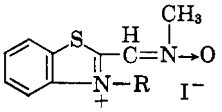
I



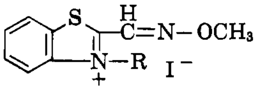
II

The studies presented in this paper are somewhat different in that five-membered rings are being methylated and the basicity of the 1-methylbenzimidazole ring is much stronger and that of the benzothiazole ring much weaker than the basicities of the pyridines and quinolines studied previously. No difficulty was found in synthesizing I in ethanol through a room temperature methylation of 1-methylbenzimidazole-2-carboxaldoxime. In contrast, the more vigorous reaction conditions of refluxing nitrobenzene–alcohol were needed in the methylation of the much less basic benzothiazole-2-carboxaldoxime. Besides II, a dimethylation product, N-methyl 2-formyl-3-methylbenzothiazolium iodide oxime (V) was isolated. It appears that the side product was formed through a methylation of II because with lower reflux temperature and longer reaction time only II was isolated.

The more facile synthesis of I than that of II is understandable in view of the stronger basic center in the 1-methylbenzimidazole ring. Failure to find 1-methylbenzimidazolium or benzothiazolium hydroiodides in which monomethylation had occurred on either the oxime nitrogen or oxygen, *e.g.*, III or IV, would indicate that the ring nitrogens were not hindered sterically to any serious extent.



III. R = H
V. R = CH₃



IV. R = H
VI. R = CH₃

The nuclear magnetic resonance spectrum of I in deuterium oxide consists of three resonances: a singlet at 522 c.p.s. (area = 1), $=C-CH=N-$, a symmetrical multiplet centered at 468 c.p.s. (area = 4), aromatic protons, and a single sharp peak at 249 c.p.s. (area = 6), $=\overset{+}{N}-CH_3$ and $-N-CH_3$ protons. The resonance at 249 c.p.s. is undoubtedly a result of the average electronic environment experienced by the two methyl groups because of the resonance of the quaternary center between the two nitrogens. The spectrum of N-methyl-2-pyridone shows a methyl resonance at 215 c.p.s. while that of 1,3,5-trimethylpyridinium iodide of 2-pyridone exhibits 1-methyl resonance at 275 c.p.s.[7] The average of these two values is 245 c.p.s., which is in good agreement with the observed frequency of the methyl groups in I. Traces of water, and possibly some exchange, precluded detection of the =NOH proton in the spectrum obtained in deuterium oxide. By the use of redistilled, dry acetonitrile, the =NOH proton resonance was observed near 740 c.p.s. (area = 1). Oxime protons generally absorb in this region in nonbonding solvents.

A nuclear magnetic resonance spectrum of II could not be obtained, because of the limited solubility of II in solvents commonly used in this work (D_2O and $CDCl_3$). Instead, structure proof was achieved on the basis of elemental analysis, neutralization equivalent, a broad OH stretching band found in the infrared absorption spectrum in potassium bromide, and an observed bathochromic shift of the long wave length

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(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) U. S. Army Chemical Research and Development Laboratories.

(3) Battelle Memorial Institute.

(4) (a) S. Ginsburg and I. B. Wilson, *J. Am. Chem. Soc.*, **79**, 481 (1957); (b) E. J. Poziomek, B. E. Hackley, Jr., and G. M. Steinberg, *J. Org. Chem.*, **23**, 714 (1958).

(5) E. Profft and G. Kruger, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **2**, 281 (1959–1960); *Chem. Abstr.*, **55**, 1607e (1961).

(6) B. E. Hackley, Jr., E. J. Poziomek, G. M. Steinberg, and W. A. Mosher, *J. Org. Chem.* **27**, 4220 (1962).

(7) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).