[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. VIII. Medium-sized Cyclic Olefins from Amine Oxides and Quaternary Ammonium Hydroxides[1,2]

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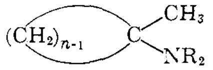
Thermal decompositions of the N-oxides derived from N,N-dimethyl-1-methylcycloalkylamines II having eight-, nine- and ten-membered rings yield olefin mixtures containing 98.6, 94.0 and 97.5%, respectively, of 1-methylcycloalkenes. Considerable amounts of the *trans* isomers are formed from the nine- and ten-membered N-oxides. Pyrolyses of the corresponding quaternary hydroxides produce mixtures of methylenecycloalkanes and 1-methylcycloalkenes (predominantly *cis*), violation of the Hofmann rule being at a maximum in the decomposition of the nine-membered quaternary hydroxide. Importance of relative product stabilities and the operation of non-bonded interactions are discussed as possible explanations for the observed directions of elimination. Thermal decompositions of the N-oxides and quaternary hydroxides of N,N-dimethylcycloalkylmethylamines IV containing eight-, nine- and ten-membered rings proceed as expected with formation of the corresponding methylenecycloalkanes.

In an earlier investigation of the course of the amine oxide pyrolysis of a number of N,N-dimethyl-1-methylcycloalkylamines (II, n = 5, 6, 7) it was



I, R = H
II, R = CH_3

III, R = H
IV, R = CH_3

shown that the olefin mixtures formed contained 97.5, 2.8 and 84.8%, respectively, of 1-methylcycloalkenes, whereas decomposition of the corresponding quaternary hydroxides (Hofmann elimination reaction yielded mainly the methylenecycloalkanes in addition to small amounts of the endocyclic isomers.[3] The results of the N-oxide pyrolyses, which differed from those obtained with acyclic amines (where the relative amounts of olefins formed were found to be nearly proportional to the numbers of β-hydrogen atoms available),[4] were interpreted in terms of the steric requirements of the various ring systems. Predominant formation of the methylenecycloalkanes in the Hofmann elimination reactions was in accordance with the Hofmann rule.[5] This study has now been extended to include the tertiary amines having eight-, nine- and ten-membered rings (II, n = 8, 9, 10). Such an investigation was expected to provide further information concerning the stereochemistry of medium-sized ring systems. The question of whether *trans* double bonds would be introduced into the rings by one or both methods also was of interest; a third objective was the preparation of eight-, nine- and ten-membered cyclic olefins for a study of the equilibria between methylenecycloalkanes and 1-methylcycloalkenes.[6] This also was the reason for including the N,N-dimethylcycloalkylmethylamines IV (n = 8, 9, 10) in the investigation.

The amines of type I were prepared by application of the Ritter reaction[7] to the olefins obtained by dehydration of the corresponding 1-methylcycloalkanols. The latter were formed by the addition of methylmagnesium iodide to cycloöctanone, cyclononanone and cyclodecanone. The low yield (39%) of 1-methylcyclodecanol in this reaction has been attributed to enolization of the cyclodecanone during addition of the Grignard reagent.[8] In an effort to suppress this side-reaction the Grignard reagent was substituted by methyllithium, but two experiments conducted at 0° and 35°, respectively, failed to improve the yield of tertiary alcohol; the same results also were obtained when the ketone was added to methylmagnesium iodide in boiling benzene. Dehydration of 1-methylcyclodecanol with sulfuric acid gave a mixture of 80% *cis*- and 20% *trans*-1-methylcyclodecene. The primary amines obtained in the Ritter reaction were methylated by the Clarke–Eschweiler method to yield the tertiary amines II. N,N-Dimethylcycloöctylmethylamine (IV, n = 8) and the corresponding ten-membered cyclic amine were prepared by reduction of the N,N-dimethylcycloalkanecarboxamides with lithium aluminum hydride. An attempt to prepare the tertiary amine IV (n = 10) by a Hofmann degradation of cyclodecylacetic acid was abandoned because the intermediate ethyl cyclodecylidenecyanoacetate could not be hydrogenated easily. Methylation of cyclononylmethylamine, obtained by reduction of cyclononanecarboxamide, with formaldehyde and formic acid gave a low yield (43%) of the tertiary amine IV (n = 9). The primary amide was used as an intermediate in this synthesis because it was a solid that could be purified by recrystallization. An over-all yield of 75% of IV (n = 9) was obtained when the primary amine was quaternized with methyl iodide and a base and the resulting methiodide reduced with lithium aluminum hydride.[9] The properties of the primary and tertiary amines prepared in this study are summarized in Table I, and those of their picrates in Table II. The amine oxides, obtained from the tertiary amines by reaction with hydrogen peroxide, were characterized as their picrates (Table IV). The methiodides of the tertiary amines (Table III) were prepared and converted to the quaternary hydroxides.

The N-oxides and methohydroxides were pyrolyzed, and the olefinic products were analyzed by gas chromatography. The results are summarized

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[1] Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

[2] Paper VII, THIS JOURNAL, **82**, 4656 (1960).

[3] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

[4] A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

[5] A. C. Cope and E. R. Trumbull, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. XI, to be published.

[6] A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, THIS JOURNAL, **81**, 3153 (1959); **82**, 1750 (1960).

[7] J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948).

[8] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[9] A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *ibid.*, **82**, 4651 (1960).

TABLE I

PRIMARY AND N,N-DIMETHYL TERTIARY AMINES

Amine	n	Yield, %	B.p., ° C.	Mm.	$n^{25}D$	d^{25}_4	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
I	8	73[a]	82–83	14	1.4729	0.8900	$C_9H_{19}N$	76.53	76.44	13.56	13.51	9.91	9.96
I	9	77[a]	52–53	0.7	1.4769	.8912	$C_{10}H_{21}N$	77.35	77.68	13.63	13.78	9.02	9.05
III	9	95[b]	69–70	.8	1.4844	.9029	$C_{10}H_{21}N$	77.35	77.27	13.63	13.76	9.02	9.05
I	10	51[a]	70–71	.8	1.4820	.8980	$C_{11}H_{23}N$	78.03	78.09	13.69	13.66	8.28	8.25
II	8	94[c]	105–106	15	1.4762	.8954	$C_{11}H_{23}N$	78.03	78.25	13.69	13.61	8.28	8.42
IV	8	87[d]	101	19	1.4658	.8708	$C_{11}H_{23}N$	78.03	77.96	13.69	13.71	8.28	8.42
II	9	95[c]	79–80	1	1.4816	.8937	$C_{12}H_{25}N$	78.61	78.69	13.75	13.74	7.64	7.83
IV	9	75[e]	77–78	1.5	1.4710	.8684	$C_{12}H_{25}N$	78.61	78.64	13.75	13.91	7.64	7.50
II	10	97[c]	87–90	0.6	1.4862	.9025	$C_{13}H_{27}N$	79.11	79.41	13.79	13.83	7.10	7.28
IV	10	86[d]	61–62	0.2	1.4748	.8741	$C_{13}H_{27}N$	79.11	79.10	13.79	13.71	7.10	7.22

[a] Based on 1-methylcycloalkene. [b] Based on cyclononanecarboxamide. [c] Based on 1-methylcycloalkylamine. [d] Based on N,N-dimethylcycloalkanecarboxamide. [e] Based on cyclononylmethylamine.

TABLE II

PRIMARY AND N,N-DIMETHYL TERTIARY AMINE PICRATES

Amine	n	M.p., ° C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I	8	187.6–188.8[a]	$C_{15}H_{22}N_4O_7$	48.64	48.56	5.99	5.78	15.13	14.85
I	9	207.0–208.6 d.[b]	$C_{16}H_{24}N_4O_7$	49.99	50.19	6.29	6.32	14.58	14.73
III	9	212.6–214.0 d.[b]	$C_{16}H_{24}N_4O_7$	49.99	50.30	6.29	6.41	14.58	14.69
I	10	212–213 d.[c]	$C_{17}H_{26}N_4O_7$	51.25	51.46	6.58	6.79	14.06	13.97
II	8	199.8–200.5[d]	$C_{17}H_{26}N_4O_7$	51.25	51.08	6.58	6.36	14.06	14.20
IV	8	118.9–119.6[e]	$C_{17}H_{26}N_4O_7$	51.25	51.26	6.58	6.58	14.06	14.24
II	9	161.6–162.2 d.[b]	$C_{18}H_{28}N_4O_7$	52.41	52.53	6.84	6.86	13.59	13.75
IV	9	110.2–111.2[b]	$C_{18}H_{28}N_4O_7$	52.41	52.59	6.84	6.84	13.59	13.37
II	10	163.6–164.6[b]	$C_{19}H_{30}N_4O_7$	53.51	53.85	7.09	7.16	13.14	13.15
IV	10	113.6–114.6[b]	$C_{19}H_{30}N_4O_7$	53.51	53.43	7.09	7.19	13.14	13.12

[a] Recrystallized from benzene. [b] Recrystallized from ethyl acetate–hexane. [c] Recrystallized from ethanol–hexane. [d] Recrystallized from ethyl acetate. [e] Recrystallized from ethanol.

TABLE III

ALKYLTRIMETHYLAMMONIUM IODIDES

Methiodides	n	Yield, %	M.p., ° C.	Formula	Carbon, %		Hydrogen, %		Iodine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
$II \cdot CH_3I$	8	88[a]	265.6–267.3[b]	$C_{12}H_{26}NI$	46.30	46.36	8.42	8.12	40.78	40.71
$IV \cdot CH_3I$	8	100[a]	250.8–252.4[c]	$C_{12}H_{26}NI$	46.30	46.35	8.42	8.14	40.78	40.94
$II \cdot CH_3I$	9	79[d]	259.4–260.0 d.	$C_{13}H_{28}NI$	48.00	47.83	8.68	8.71	39.02	38.65
$IV \cdot CH_3I$	9	93[e]	259.2–259.8 d.[f]	$C_{13}H_{22}NI$	48.00	48.27	8.68	8.93	39.02	39.10
$II \cdot CH_3I$	10	93[d]	259.6–260.4 d.	$C_{14}H_{30}NI$	49.55	49.22	8.91	8.97	37.41	37.55
$IV \cdot CH_3I$	10	96[a]	261.8–262.2 d.[g]	$C_{14}H_{30}NI$	49.55	49.52	8.91	8.73	37.41	37.56

[a] A mixture of the tertiary amine and excess methyl iodide in ether was stored at room temperature for four days and the methiodide was collected on a filter. [b] Recrystallized from methanol–acetone. [c] Recrystallized from ethyl acetate–acetone. [d] A mixture of the tertiary amine and excess methyl iodide in methanol was heated under reflux overnight; the methanol and excess methyl iodide were removed by distillation under reduced pressure and the residue was recrystallized from methanol–ethyl acetate (two crops). [e] Prepared by treatment of cyclononylmethylamine with methyl iodide and sodium bicarbonate (ref. 9). [f] Recrystallized from chloroform–ethyl acetate. [g] Recrystallized from chloroform–hexane.

TABLE IV

N,N-DIMETHYL TERTIARY AMINE OXIDE PICRATES

Amine	n	Yield, %	M.p., ° C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
IV	8	90	141–142[a]	$C_{17}H_{26}N_4O_8$	49.27	49.26	6.32	6.29	13.52	13.29
II	9	31–37[b]	132–133[c]	$C_{18}H_{28}N_4O_8$	50.46	50.73	6.59	6.81	13.08	13.37
IV	9	85–87	122.4–123.2[c]	$C_{18}H_{28}N_4O_8$	50.46	50.46	6.59	6.54	13.08	13.18
II	10	69[b]	133.4–134.0[d]	$C_{19}H_{30}N_4O_8$	51.57	51.83	6.83	6.80	12.66	12.72
IV	10	92	102.6–103.2[e]	$C_{19}H_{30}N_4O_8$	51.57	51.60	6.83	6.92	12.66	12.52

[a] Recrystallized from ethanol. [b] A portion of the amine oxide had decomposed before the oxidation of the amine was complete. [c] Recrystallized from ethyl acetate–hexane. [d] Recrystallized from aqueous ethanol. [e] Recrystallized from a mixture of ethanol, ether and pentane.

in Tables V and VI. The amine oxide derived from N,N-dimethyl-1-methylcyclooöctylamine (II, n = 8) had decomposed completely before the oxidation of the amine was complete. N,N-Dimethyl-1-methylcyclooöctylamine formate was isolated from this reaction in 25% yield in addition to a 56% yield of an olefin mixture. Formation of the formate was avoided when the oxidation was carried out in the presence of sodium carbonate. Since the composition of the olefin mixture was close to the equilibrium composition of methylenecyclooöctane and 1-methylcyclooöctene it was possible that some of

Table V

Olefins Obtained from Amine Oxides and Trimethylammonium Hydroxides of $\underline{\overline{(CH_2)_{n-1}C}}(CH_3)N(CH_3)_2$

Amine oxides; n =	Temp. of decomp., ° C.	Ave. yield, %[a] Olefins	Ave. yield, %[a] Amine	Composition of olefin mixture in weight % Exocyclic	Endocyclic *cis*	Endocyclic *trans*
8	25[b]	56	4	3.5	96.5	0
8[d]	25[b]	84[e]	0	1.4	98.6	0
9	60–100[f]	72	8	6.0[g]	81.8[h]	12.2[h]
10	65–85[f]	86	1	2.5[g,h]	63.5[h]	34.0[h]
Trimethyl-ammonium hydroxides, n =						
8	80–90	82	7	63.5	36.5	0
9	85–100	83	0	48.0	51.0	1.0
10		92	0	66.4	31.4	2.2

[a] Average of two or more experiments. [b] The amine oxide decomposed completely during the oxidation of the tertiary amine. [c] In addition, N,N-dimethyl-1-methylcycloöctylamine formate was isolated in 25% yield. [d] The amine was oxidized in the presence of sodium carbonate. [e] B.p. 80–81° (52 mm.), n^{25}D 1.4678; A. C. Cope and H. C. Campbell, THIS JOURNAL, **74,** 179 (1952), report b.p. 87–90° (84 mm.), n^{25}D 1.4682. [f] A portion of the amine oxide had decomposed before oxidation of the amine was complete. [g] Composition of the olefin mixture obtained from pyrolysis of that portion of the amine oxide which had not decomposed during oxidation of the amine. [h] See Table VII. [i] Not determined.

Table VI

Olefins Obtained from Amine Oxides and Trimethylammonium Hydroxides of $\underline{\overline{(CH_2)_{n-1}}}\,CHCH_2N(CH_3)_2$

Amine oxides, n =	Temp. of decomp., ° C.	Average yield, %[a] Olefins	Average yield, %[a] Amines	Composition of olefin mixture in weight % Exocyclic	Endocyclic[b]	Other[c]
8	125–130	79[d]	6[c]	100	0	0
9	100–120	80[e]	4	98.2	0	1.8
10	110–140	74[f]	15	100	0	0
Trimethyl-ammonia hydroxides, n =						
8	95–110	83	7	98.8	0.5	0.7
9	140–180	71	15	96.0	4.0	0
10	110–130	74	16	98.1	1.9	0

[a] Average of two or more experiments. [b] Identified only by retention time on gas chromatography. [c] Not identified. [d] B.p. 60° (18 mm.), n^{25}D 1.4703, d^{25}_{4} 0.8548; F. Šorm and J. Beranek, *Chem. Listy*, **47,** 708 (1953); *C.A.*, **49,** 194 (1955), report b.p. 155°, n^{20}D 1.4682, d^{20}_{4} 0.8485. [e] B.p. 69–70° (10 mm.), n^{25}D 1.4782; F. Šorm and J. Beranek, (ref. *d*) report b.p. 169°, n^{19}D 1.4808. [f] See Table VII.

Table VII

Hydrocarbons

Compounds[a]	Purity, %[b]	B.p. ° C. (mm.)	n^{25}D	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
trans-1-Methylcyclononene	95	[c]	1.4791	$C_{10}H_{18}$	86.88	86.64	13.12	13.40
cis-1-Methylcyclononene[d]	95.2	77–78 (16)	1.4788	$C_{10}H_{18}$	86.88	86.70	13.12	13.10
Methylenecyclodecane	100	69–70 (4)	1.4822	$C_{11}H_{20}$	86.76	86.60	13.24	13.35
trans-1-Methylcyclodecene	97.9	[c]	1.4848	$C_{11}H_{20}$	86.76	86.73	13.24	13.38
cis-1-Methylcyclodecene	98.7	[c]	1.4843	$C_{11}H_{20}$	86.76	86.77	13.24	13.04
Methylcyclononane[e]	99	[c]	1.4600	$C_{10}H_{20}$	85.63	85.53	14.37	14.39
Methylcyclodecane[e]	99	[c]	1.4662	$C_{11}H_{22}$	85.63	85.58	14.37	14.36

[a] The samples of olefins were obtained from the corresponding tertiary amines (see Tables V and VI and Experimental section) unless otherwise stated. [b] As determined by gas chromatography. [c] Boiling points were not determined because of lack of material. [d] Prepared by dehydration of 1-methylcyclononanol (see Experimental section). [e] See Experimental section.

the 1-methylcycloöctene had been formed by isomerization of the exocyclic isomer. However, experiment showed that methylenecycloöctane is stable under the conditions of the oxidation. The N-oxides derived from the nine- and ten-membered cyclic amines of type II partly decomposed during the oxidation.

The structures of the olefins newly prepared in this study (Table VII) were assigned on the basis of the mode of formation, their infrared spectra, their tendency to form complexes with silver nitrate, their behavior in the presence of acid and by hydrogenation to methylcycloalkanes. Both *cis*-cyclooctene and *cis*-cyclodecene are known[10] to have two $-CH_2-$ deformation frequencies in the infrared region of 1400–1500 cm.$^{-1}$ whereas the *trans* isomers of both compounds have only one band in this area. The three isomeric *cis-cis*-cycloöctadienes have at least two bands in this region[11] while the two known *cis-trans*-cycloöctadienes have only one.[11,12] All the olefins encountered in this study having nine- and ten-membered rings had either two or three

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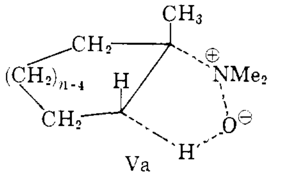
[10] N. L. Allinger, THIS JOURNAL, **80,** 1953 (1958).

[11] A. C. Cope and C. F. Howell, to be published.

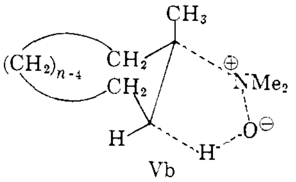
[12] A. C. Cope and C. L. Bumgardner, THIS JOURNAL, **78,** 2812 (1956).

bands in the 1400–1500 cm.$^{-1}$ region except *trans*-1-methylcyclononene and *trans*-1-methylcyclodecene, which had only one. The compound assigned the structure of *trans*-1-methylcyclononene was found to be much more soluble in silver nitrate solutions than the *cis* isomer; also, it was so strongly retained on a gas chromatographic column containing a solution of silver nitrate in tetraethylene glycol at 90° that it was not eluted with helium within a reasonable time for analysis. *trans*-1-Methylcyclodecene was retained on this column about twice as long as the *cis*-isomer. Faster elution of *trans*-1-methylcyclodecene than its nine-membered homolog is to be expected since the latter is more highly strained and consequently forms a more stable silver nitrate complex. Treatment of *trans*-1-methylcyclononene with *p*-toluenesulfonic acid resulted in complete isomerization to the *cis* isomer, whereas the ten-membered homolog under these conditions gave the equilibrium mixture containing 99.4% of *cis*- and 0.6% of *trans*-1-methylcyclodecene (see ref. 6, Table I). Methylenecyclononane and *cis*- and *trans*-1-methylcyclononene each absorbed one mole of hydrogen on catalytic reduction forming methylcyclononane. The corresponding isomers in the ten-membered series also contained only one double bond according to hydrogenation data, and gave methylcyclodecane as the only reduction product.[13] Gas chromatography using stationary phases which separated *cis*- and *trans*-1-methylcyclononene failed to reveal the presence of *trans*-1-methylcyclooctene (which is as yet unknown) among the products of the pyrolyses of the N-oxide or methohydroxide of N,N-dimethyl-1-methylcycloöctylamine.

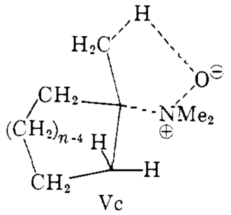
The compositions of the olefin mixtures obtained from the N,N-dimethyl-1-methylcycloalkylamines by the Hofmann elimination reaction and the amine oxide pyrolysis (Table V) reflect the differences in mechanism[5] between these two reactions. The N-oxide pyrolysis proceeds through a planar quasi five-membered transition state involving the $N^{\oplus}$–$O^{\ominus}$ function, a β-hydrogen atom and two carbon atoms. In amines of type II, seven β-hydrogen atoms are available for elimination: three on the C_1-methyl group (giving rise to methylene-cycloalkane), two *cis*[14]-β-hydrogen atoms on the ring (leading to *cis*-1-methylcycloalkene) and two *trans*[14]-β-hydrogen atoms (yielding *trans*-1-methylcycloalkene). The composition of the olefin mixtures (Table V) shows that the direction of elimination in N-oxides of amines of type II is not determined by the number of hydrogen atoms available (as is the case in acyclic amines[4]). Obviously, the cyclic transition state leading to the *cis*-1-methylcycloalkene (Va) must be energetically favored over the ones leading to the *trans* isomer Vb and to the methylenecycloalkane Vc. A model of N,N-dimethyl-1-methylcyclodecylamine N-oxide shows that in the transition state leading to *trans*-1-methylcyclodecene (Vb, $n = 10$) there is more non-bonded interaction between the C_1-methyl group and hydrogen atoms across the ring than in Va ($n = 10$). This interaction becomes more serious in the smaller rings; in the case of the eight-membered amine (II, $n = 8$), a model of the transition state leading to the *trans* isomer cannot be constructed at all. It is interesting to note that N,N-dimethylcycloöctylamine gives *cis*-cycloöctene when subjected to the amine oxide pyrolysis,[15] whereas the *trans* isomers are obtained from the corresponding nine- and ten-membered amines.[16] It has been noted before that introduction of a methyl group (on C_1) increases the steric strain in *trans*-cycloalkenes relative to their *cis* isomers.[6]



Va



Vb



Vc

The fact that only small amounts of the methylenecycloalkanes are formed in all three cases cannot be explained as readily on the basis of the steric requirements of the transition states. Models show no steric interaction which would clearly favor Va over Vc. The predominant formation of 1-methylcyclopentene in the pyrolysis of the *N*-oxide of N,N-dimethyl-1-methylcyclopentylamine (II, $n = 5$) has been explained by pointing out that elimination *via* Va ($n = 5$) requires orientation of the $N^{\oplus}$–$O^{\ominus}$ bond only, whereas attainment of transition state Vc necessitates orientation of a C–H bond of the C_1-methyl group and the amine oxide bond.[3] Some of the factors that influence product stability may also be important in determining the direction of elimination. The equilibria between the methylenecycloalkanes and the 1-methylcycloalkenes in the eight-, nine- and ten-membered cyclic olefins are almost completely on the sides of the endocyclic isomers.[6] Formation of an endocyclic double bond introduces two trigonal centers into the ring (methylenecycloalkanes have only one trigonal ring carbon atom) and thus provides more relief of the steric strain associated with medium-sized rings. An indication of the magnitude of this strain, which is enhanced by the bulky amine oxide function and the C_1-methyl group, is the fact that the N-oxides of amines of type II investigated in this study all decompose partly or completely at room temperature.[17,18]

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(13) This finding is of importance because A. T. Blomquist and P. R. Taussig, THIS JOURNAL, **79**, 3505 (1957), found 1,8-nonadiene among the products of the pyrolysis of cyclononyl acetate, *trans*-cyclononene probably being an intermediate.

(14) Position relative to the amine function.

(15) A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

(16) A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

(17) Decomposition of N-oxides usually occurs at 100–200°. Decomposition at room temperature also was observed with the N-oxides of N,N-dimethyl-*cis*-9-decalylamine, N,N-dimethyl-2,2-di-*t*-butylethylamine and N,N-dimethyltriethylmethylamine.

(18) A. C. Cope, E. M. Acton, Z. Jacura and D. L. Ross, unpublished results.

Pyrolysis of the methohydroxides of N,N-dimethyl-1-methylcycloalkylamines (II, $n = 8, 9, 10$) produces mixtures of methylenecycloalkanes (the products predicted on the basis of the Hofmann rule[5]) and 1-methylcycloalkenes (Table V). Violation of the Hofmann rule was greatest in the methohydroxide of the nine-membered amine. The Hofmann elimination reaction usually[5] proceeds by a bimolecular (E2) *trans* elimination reaction; in the transition state the quaternary ammonium group and a β-hydrogen atom are in an anti-planar arrangement. The steric (and possible electronic) effects[5] that determine the direction of elimination toward formation of the least substituted olefin may be opposed by two effects in the case of methohydroxides of amines of type II: increased importance of product stabilities, as discussed for the N-oxide pyrolyses, and a shielding of the β-hydrogen atoms on the methyl group by hydrogen atoms across the ring, which would render the approach of the base (hydroxide ion) more difficult. Such a shielding effect may also be partly responsible for the fact that *trans*-1-methylcycloalkenes are formed to a lesser extent in the Hofmann elimination reaction than in the pyrolysis of the N-oxides of these amines. In addition, attainment of the transition state leading to the formation of the *trans*-olefin, in which a *cis*[14]-β-ring hydrogen atom has to become *anti* and coplanar with the amino function, is opposed by steric interaction of the C_1-methyl group with hydrogen atoms across the ring. This is especially true of the eight- and nine-membered amines (II, $n = 8,9$).[19]

Pyrolysis of the N-oxides and quaternary hydroxides of the N,N-dimethylcycloalkylmethylamines (IV, $n = 8, 9, 10$) proceeds normally with formation of the corresponding methylenecycloalkanes (Table VI).

The fact that a considerable amount of the formate of N,N-dimethyl-1-methylcycloöctylamine was isolated from the oxidation of this amine may be rationalized by assuming that the N,N-dimethylhydroxylamine formed in the room temperature elimination of the N-oxide was oxidized by the hydrogen peroxide present in excess, giving rise to formic acid, which in turn formed a salt with unoxidized tertiary amine. Possible intermediates in the oxidation of N,N-dimethylhydroxylamine are a nitrone and formaldehyde.[20] The formate, as isolated from the reaction mixture, was a viscous liquid that could be distilled under reduced pressure. The amount of formic acid present in the salt was found to be 1.77 moles per mole of tertiary amine. The low carbon values obtained in the combustion analysis as well as the presence of a carbonyl peak at 1725 cm.$^{-1}$ in the infrared spectrum were in accord with this finding. Formates of tertiary amines that can be distilled have been observed before. André[21] found that trimethylamine formed a salt with formic acid that had the composition $2N(CH_3)_3 \cdot 5\ HCOOH$ which could be distilled under reduced pressure without change of the composition; in the vapor phase this salt was found to be completely dissociated.

Experimental[22]

1-Methylcycloalkenes were prepared by addition of methylmagnesium iodide[8] to cycloöctanone,[23] cyclononanone (obtained in 66% yield by reduction of azeoloin with zinc by the method of ref. 24) and cyclodecanone[24] followed by acid-catalyzed dehydration of the resulting 1-methylcycloalkanols. 1-Methylcycloöctanol was dehydrated (without prior isolation) with *p*-toluenesulfonic acid[25]; 1-methylcycloöctene, b.p. 96–97.5° (100 mm.), n^{25}D 1.4672–1.4687 (lit.[26] b.p. 87–90° at 84 mm., n^{25}D 1.4682) was obtained in 84% yield (based on cycloöctanone). 1-Methylcyclononanol, obtained in 65% yield, m.p. 50.5–51.7° (lit.[8] m.p. 51–52°), was dehydrated by slow steam-distillation from twice the amount by volume of 30% sulfuric acid. The steam distillate was saturated with sodium sulfate and the olefin layer separated. The aqueous layer was then extracted three times with ether; the ether extracts were combined with the olefin layer and dried over sodium sulfate. Distillation gave a 95% yield of 1-methylcyclononene, the physical properties of which are listed in Table VII. Addition of methylmagnesium iodide to cyclodecanone gave a 37–44% yield of 1-methylcyclodecanol, m.p. 50–53° after one crystallization from pentane at −10° (lit.[8] m.p. 52.5–53.1°). The concentrated mother liquors containing unreacted cyclodecanone were recycled twice raising the overall yield of 1-methylcyclodecanol to 67%. Treatment of cyclodecanone with methyllithium at 35°, or with methylmagnesium iodide in refluxing benzene, failed to improve the yield of 1-methylcyclodecanol (which was 37 and 39%, respectively). 1-Methylcyclodecanol was dehydrated as described above for the dehydration of the nine-membered alcohols. The resulting product that was obtained in 77% yield, b.p. 68° (4 mm.), n^{25}D 1.4843, was a mixture of 80% *cis*- and 20% *trans*-1-methylcyclodecene as shown by gas chromatography using a 52% solution of silver nitrate in tetraethylene glycol (30% on firebrick) as the stationary phase. This mixture was used without further separation for the preparation of 1-methylcyclodecylamine.

1-Methylcycloalkylamines.—The 1-methylcycloalkenes were converted to the 1-methylcycloalkylamines by the previously described[3] modification of the method of Ritter and Kalish.[7] The yields and physical properties of the amines so obtained are listed in Table I and those of their picrates in Table II. When 1-methylcyclodecanol was used instead of the olefin, the yield of amine was only 8%.

N,N-Dimethyl-1-methylcycloalkylamines.—The 1-methylcycloalkylamines were methylated by the Clarke–Eschweiler method[27]; the yields and physical properties of the

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[19] Pyrolysis of N,N,N-trimethylcycloöctylammonium hydroxide yields a 60/40 mixture of *trans*- and *cis*-cycloöctene (ref. 15); the *trans* isomers are obtained almost exclusively from the corresponding nine- and ten-membered quaternary hydroxides (ref. 16).

[20] No information concerning the oxidation of N,N-dimethylhydroxylamine could be found in the literature. However, W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 1004 (1899), found that dimethylamine, on treatment with hydrogen peroxide, gave rise to formic acid, among other products. Diethylamine and di-*n*-propylamine yielded the corresponding N,N-dialkylhydroxylamines under these conditions. Nitrones have been isolated as intermediates in the oxidation of aromatic hydroxylamines. These intermediates could be hydrolyzed to aldehydes [*cf.* for example J. Thesing, *Chem. Ber.*, **87**, 507 (1954); J. Thesing, A. Müller and G. Michel, *ibid.*, **88**, 1027 (1955)]. More recently, D. H. Johnson, M. A. T. Rogers and G. Trappe, *J. Chem. Soc.*, 1093 (1956), reported evidence for the intermediate formation of nitrones in the autoxidation of aliphatic dialkylhydroxylamines.

[21] G. André, *Compt. rend.*, **126**, 1105 (1898).

[22] Melting points are corrected and boiling points are uncorrected. The infrared spectra were obtained with a Perkin–Elmer recording spectrophotometer, model 21, using a sodium chloride cell. Gas chromatographic analyses were carried out using 190 × 0.8-cm. Pyrex columns containing the stationary phase (as specified) on 48–100 mesh firebrick. The samples were eluted with helium at 15 p.s.i. and detected with a thermal conductivity cell. We are indebted to Dr. S. M. Nagy for microanalyses and to Mrs. N. Alvord for spectral determinations.

[23] A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5887 (1952).

[24] A. C. Cope, J. W. Barthel and R. D. Smith, *Org. Syntheses*, **36**, 14 (1956).

[25] G. Chavanne and L. Vogel, *Bull. soc. chim. Belge*, **37**, 141 (1928).

[26] A. C. Cope and H. C. Campbell, THIS JOURNAL, **74**, 179 (1952).

[27] R. N. Icke and B. B. Wisegarver, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 723.

N,N-dimethyl-1-methylcycloalkylamines so obtained are summarized in Table I, and those of their picrates in Table II. The methiodides are listed in Table III.

N,N-Dimethylcycloöctanecarboxamide.—Cycloöctanecarboxylic acid[28] was converted to N,N-dimethylcyclooctanecarboxamide by treatment of the acid chloride with dimethylamine by the method described for a similar case.[29] The yield of the amide, b.p. 92° (0.15 mm.), was 96%.

Cyclononanecarboxamide.—Cyclodecanone (10 g.) was brominated with N-bromosuccinimide and the α-bromoketone was rearranged by treatment with sodium methoxide in methanol at −20° as described previously.[30] Water (10 ml.) was added and the mixture was heated under reflux for 30 min. to hydrolyze the methyl ester. The mixture was extracted continuously with ether for 1 day to remove neutral compounds completely and then acidified. In three similar preparations, an average yield of 6.9 g. (62%) of crude cyclononanecarboxylic acid was obtained. Three reactions on a 50-g. scale yielded an average of only 38% of the acid. The cyclononanecarboxylic acid was characterized as the anilide, which melted at 140.4–141.6° after sublimation and two recrystallizations from methanol (lit.[30] m.p. 140–141°). Cyclononanecarboxamide was prepared by treatment of cyclononylcarbonyl chloride with ammonia.[31] The crude amide was dissolved in acetone, precipitated with water, sublimed under reduced pressure at 120° and then recrystallized three times from chloroform to give colorless plates, m.p. 176.0–176.8°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32. Found: C, 71.12; H, 11.42.

A sample of cyclononanecarboxylic acid prepared by carbonation of cyclononylmagnesium bromide[28] was converted to the amide which melted at 174.8–176.0° after three crystallizations from chloroform. The melting point was undepressed by admixture with cyclononanecarboxamide described above.

Cyclononylmethylamine.—Cyclononanecarboxamide (25.5 g.) was placed in a Soxhlet extractor attached to a three-necked flask containing a suspension of 19.7 g. (3 equivalents) of lithium aluminum hydride in 490 ml. of anhydrous ether.[32] The mixture was stirred and refluxed for 76 hr. so that the amide was gradually added to the hydride mixture. The excess hydride was decomposed with 115 ml. of ethanol, and 250 ml. of water containing 160 g. of sodium hydroxide was added. The resulting suspension was steam distilled until the distillate was neutral. The distillate was acidified with concentrated hydrochloric acid and extracted with ether. The aqueous layer was made basic with sodium hydroxide and the liberated amine was extracted with ether, dried over sodium sulfate, concentrated and distilled through a semi-micro column to give 24.2 g. (95%) of cyclononylmethylamine with the properties listed in Table I. The picrate is listed in Table II.

N,N-Dimethylcyclodecanecarboxamide was prepared in 89% yield from cyclodecanecarboxylic acid[28] *via* the acid chloride.[29] The amide had b.p. 95.0–96.5° (0.05 mm.), d^{25}_{4} 0.9636, $n^{25}D$ 1.4951.

Anal. Calcd. for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 74.12; H, 11.94; N, 6.65.

N,N-Dimethylcycloalkylmethylamines.—N,N-Dimethylcycloöctylmethylamine and N,N-dimethylcyclodecylmethylamine were prepared by reduction of the corresponding N,N-dimethylcycloalkanecarboxamides with lithium aluminum hydride.[29] The ether extract of the acidified steam distillate from the reduction of N,N-dimethylcyclodecanecarboxamide was dried and concentrated. Distillation of the residue gave a 5% yield of an alcohol, b.p. 100° (0.95 mm.), the infrared spectrum of which was consistent with its formulation as cyclodecylmethanol. Alcohols have been found previously among the products of the lithium aluminum hydride reduction of disubstituted amides.[33]

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.27; H, 12.94.

A small sample of the alcohol in hexane was warmed with an excess of *p*-nitrobenzoyl chloride and then stored with 5% aqueous sodium bicarbonate for 1 month, during which time the product slowly crystallized. Four recrystallizations from pentane gave pure cyclodecylmethyl *p*-nitrobenzoate, m.p. 48.6–49.0°.

Anal. Calcd. for $C_{18}H_{25}NO_4$: C, 67.79; H, 7.89. Found: C, 68.01; H, 7.97.

N,N-Dimethylcyclononylmethylamine was prepared in 80% yield by reduction of N,N,N-trimethylcyclononylmethylammonium iodide with lithium aluminum hydride.[9] The methiodide was obtained in 93% yield by quaternization of cyclononylmethylamine.[9] Direct methylation of cyclononylmethylamine by the Clarke–Eschweiler method[27] gave the tertiary amine in only 43% yield. The yields and physical properties of the N,N-dimethylcycloalkylmethylamines are summarized in Table I, those of their picrates in Table II. The methiodides are listed in Table III.

Ethyl Cyclodecylidenecyanoacetate.—Cyclodecanone (19.25 g.), 28.1 g. of ethyl cyanoacetate, 6 g. of acetic acid, 50 ml. of benzene and 1.7 g. of ammonium acetate were heated under reflux using a modified Dean–Stark water separator.[34] Three additional grams of ammonium acetate was added in one-gram portions after reflux periods of 3 or 4 hr. After 11 more hr. of heating, another gram of ammonium acetate was added. The mixture was cooled after a total reflux time of 25 hr., extracted three times with water and dried over sodium sulfate. The benzene was removed by distillation under reduced pressure and the residue fractionally distilled through a short Vigreux column. After a large forerun of ethyl cyanoacetate, 24.6 g. (78%) of ethyl cyclodecylidenecyanoacetate, b.p. 132–134° (0.35 mm.), $n^{25}D$ 1.4971–1.4999, was collected. Carbonyl bands at 1744 and 1728 cm.$^{-1}$ in the infrared spectrum indicated that the product was a mixture of α,β- and β,γ-unsaturated esters.

Anal. Calcd. for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30. Found: C, 71.95; H, 9.05.

This material could not be smoothly hydrogenated with 10% palladium-on-charcoal either in the presence or absence of hydrochloric acid.

Amine Oxides.—The tertiary amines were oxidized with 30% aqueous hydrogen peroxide in methanol, and the excess hydrogen peroxide was decomposed with platinum black.[35] Aliquots of the filtered amine oxide solutions were added to one equivalent of picric acid in alcohol or water; the amine oxide picrates so obtained are listed in Table IV. The N-oxides of N,N-dimethyl-1-methylcyclononylamine and N,N-dimethyl-1-methylcyclodecylamine decomposed partly before the oxidation was complete. The olefins formed in this way were isolated by concentrating the amine oxide solution (after removal of the excess hydrogen peroxide) at room temperature, using a rotary evaporator. The pressure was gradually lowered to 0.1 mm. The distillate, containing water, methanol and the olefin, was collected in a trap cooled with Dry Ice–acetone; it was diluted with water, and extracted three times with pentane. The combined extracts were dried with magnesium sulfate and distilled. The yields of olefins reported in Table V include the olefins obtained in this way. The residue from the concentration of the amine oxide solution was pyrolyzed as described below. N,N-Dimethyl-1-methylcycloöctylamine N-oxide decomposed completely during the oxidation. The olefinic products were isolated as described above; the residue, on heating under reduced pressure, distilled without decomposition, yielding 4% of N,N-dimethyl-1-methylcycloöctylamine, b.p. 47–48° (0.3 mm.), $n^{25}D$ 1.4665, and 25% of N,N-dimethyl-1-methylcycloöctylamine formate, a viscous liquid, b.p. 72–74° (0.3 mm.), $n^{25}D$ 1.4810–1.4819. The compound gave a picrate, m.p. 198°, undepressed by admixture with an authentic sample of N,N-dimethyl-1-methylcycloöctylamine picrate. A solution of 0.409 g. of the formate in 5 ml. of distilled water was passed through a column packed

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[28] A. C. Cope and L. J. Fleckenstein, THIS JOURNAL, to be published.

[29] A. C. Cope and E. Ciganek, *Org. Syntheses*, **39**, 40 (1959).

[30] K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953).

[31] R. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

[32] F. Wessely and W. Svoboda, *Monatsh.*, **82**, 621 (1951).

[33] H. E. Baumgarten, F. A. Bower and T. T. Okamoto, THIS JOURNAL, **79**, 3145 (1957), and references cited there.

[34] E. J. Cragoe, C. M. Robb and J. M. Sprague, *J. Org. Chem.*, **15** 381 (1950).

[35] The general method is described by A. C. Cope and E. Ciganek, *Org. Syntheses*, **39**, 40 (1959).

with 20–50 mesh Dowex 50-X10 ion exchange resin and eluted with water. The resulting solution was neutralized with phenolphthalein as indicator. The amount of 0.2 *N* sodium hydroxide solution required (14.5 ml.) corresponded to 0.133 g. of formic acid (1.77 moles of acid per mole of tertiary amine). The neutralized solution was concentrated to dryness using a rotary evaporator, and the residue was washed with acetone and dried at 0.1 mm., yielding 0.175 g. of white crystals, the infrared spectrum of which (in a potassium bromide pellet) was identical with that of an authentic sample of sodium formate. Formation of the amine formate was avoided by oxidizing the amine in the presence of three equivalents of sodium carbonate.

Quaternary ammonium hydroxides were prepared from the methiodides as previously described.[4]

Pyrolysis of Amine Oxides and Quaternary Ammonium Hydroxides.—An aqueous solution containing 0.03 to 0.05 mole of the N-oxide or methohydroxide was concentrated and decomposed as described previously.[3] The product was dissolved in 50 ml. of cold pentane and washed as rapidly as possible with cold 50-ml. portions of 10% hydrochloric acid, 5% sodium bicarbonate solution and water. The pentane solution containing the olefins was dried over magnesium sulfate, filtered and distilled without fractionation through a semi-micro column. Small samples obtained before extraction, before drying and after distillation served for the gas chromatographic analyses, which were averaged and are reported in Tables V and VI. The aqueous washings were extracted twice with pentane and made basic with sodium hydroxide. The liberated amines were taken up in pentane, dried with sodium sulfate and distilled. The recovered amine in each case had a refractive index agreeing closely with that of the original amine. Treatment with acid was avoided in the isolation of the eight-membered cyclic olefins; they were separated from recovered tertiary amine by distillation.

Olefins.—The olefins newly prepared in this study are listed in Table VII. *trans*-1-Methylcyclononene was obtained from the olefinic products of the pyrolysis of N,N-dimethyl-1-methylcyclononylamine N-oxide. The olefin mixture (2.5 g.) was dissolved in 50 ml. of pentane and extracted twice with 50 ml. of a 50% aqueous silver nitrate solution. The silver nitrate solutions containing most of the *trans*-olefin were added to 350 ml. of cold concentrated ammonium hydroxide and extracted with pentane. The product, *trans*-1-methylcyclononene of 67% purity, was further purified by preparative gas chromatography at 90° using 4-methyl-4-nitropimelonitrile[36] (30% on firebrick) as the stationary phase. The collected material was distilled through a micro-distillation apparatus. Methylenecyclodecane was obtained analytically pure by pyrolysis of N,N-dimethylcyclodecylmethylamine N-oxide (Table VI). *cis*- and *trans*-1-methylcyclodecene were isolated from the products of the pyrolysis of N,N-dimethyl-1-methylcyclodecylamine N-oxide (Table V) by preparative gas chromatography at 90° using a 52% solution of silver nitrate in tetraethylene glycol (30% on firebrick) as the stationary phase.

Methylcycloalkanes.—Samples (0.002 mole) of the olefins produced by several of the elimination reactions were hydrogenated in the presence of 50 mg. of prereduced platinum oxide in 3 ml. of glacial acetic acid; 0.002 mole of hydrogen was taken up in each case. The mixtures were filtered, made basic with 2.4 g. of sodium hydroxide in a small amount of water, and extracted with two portions of pentane. The products were dried with magnesium sulfate and distilled in a micro-distillation apparatus. The olefin mixtures obtained by pyrolysis of N,N-dimethyl-1-methylcyclononylamine N-oxide (Table V) and of N,N-dimethylcyclononylmethylamine methohydroxide (Table VI) gave 67 and 86%, respectively, of methylcyclononane. Methylcyclodecane (70–86% yield) was obtained by hydrogenation of the olefinic products of the pyrolyses of the N-oxide and methohydroxide of N,N-dimethyl-1-methylcyclodecylamine (Table V) and of N,N-dimethylcyclodecylmethylamine methohydroxide (Table VI). The physical properties of the two methylcycloalkanes are listed in Table VII.

Stability of Methylenecycloöctane under the Conditions of the Oxidation.—To a mixture of 0.50 g. of N,N-dimethylcycloöctylmethylamine, 0.20 g. of methylenecycloöctane and 1 ml. of methanol was added 1.0 g. of 30% hydrogen peroxide solution. After stirring at room temperature for 48 hr. the excess hydrogen peroxide was destroyed by stirring the mixture with platinum black for 12 hr. The olefin was separated from the solution containing the N-oxide of N,N-dimethylcycloöctylmethylamine (which is stable at room temperature) by extraction with pentane. Analysis of the dried pentane solution by gas chromatography showed that no isomerization of the methylenecycloöctane to its endocyclic isomer had occurred. This experiment was repeated with the exception that N,N-dimethyl-1-methylcycloöctylamine was oxidized instead of N,N-dimethylcycloöctylmethylamine. The resulting olefin mixture was composed of 51% of methylene cyclooctane and 49% of 1-methylcycloöctene. The calculated olefin composition, assuming that the N,N-dimethyl-1-methylcycloöctylamine on oxidation gave a 56% yield of 1-methylcycloöctene and that the added methylenecycloöctane did not rearrange during the oxidation, is 50% each of methylenecycloöctane and 1-methylcycloöctene.

CAMBRIDGE, MASS.

[36] H. A. Bruson, U. S. Patent 2,361,251; *C.A.*, **39**, 2079 (1945).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC., WILMINGTON 98, DEL.]

The Wittig Reaction as a Polymerization Method[1a]

BY RICHARD N. MCDONALD AND TOD W. CAMPBELL[1b]

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p-Xylylene-bis-(triphenylphosphonium chloride) reacted with terephthalaldehyde in the presence of lithium ethylate to yield a decamer of poly-*p*-xylylidene (II, $n = 9$, X = CHO). Treatment of (2-methoxy-5-methylalbenzyl)-triphenylphosphonium chloride with base produced the methoxy derivative of poly-*m*-xylylidene (V). (*p*-Hydroxyphenyl)-triphenylphosphonium bromide on treatment with base failed to yield poly-*p*-phenylene.

In recent work employing the Wittig reaction for the preparation of distyrylbenzenes,[2] diarylbutadienes[3] and 1,4-bis-(arylbutadienyl)-benzenes,[3] it became evident from the excellent yields in many of these syntheses that the Wittig reaction might lend itself to the preparation of polymers if suitable intermediates could be prepared. The polymers would be poly-xylylidenes which have not been reported in the literature, though the saturated poly-

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[1] (a) Paper III in the series "Synthesis of Hydrocarbon Derivatives by Wittig Synthesis." (b) To whom requests for reprints should be sent.

[2] T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

[3] R. N. McDonald and T. W. Campbell, *ibid.*, **24**, 1969 (1959).