TABLE I

PHOSPHINIC ACIDS RR'PO₂H

R	R'	Yield, %	M.p.,[a] °C.	Formula	P analyses, % Calcd.	P analyses, % Found	Neutral equivalent[b] Calcd.	Neutral equivalent[b] Found	N analyses, % Calcd.	N analyses, % Found
C_6H_5	C_6H_5	42[c]	192–195	$C_{12}H_{11}O_2P$	14.20	14.10	218.2	219.3		
m-ClC_6H_4	C_6H_5	27[c]	159–162	$C_{12}H_{10}ClO_2P$	12.26	12.21	252.6	252.4		
o-BrC_6H_4	C_6H_5	15[c]	206–209	$C_{12}H_{10}BrO_2P$	10.43	10.39	297.1	299.2		
m-$NO_2C_6H_4$	C_6H_5	36[c]	166–167	$C_{12}H_{10}NO_4P$	11.77	11.81	263.2	263.4	5.32	5.22
p-$NO_2C_6H_4$	C_6H_5	30[c]	153–154	$C_{12}H_{10}NO_4P$	11.77	11.59	263.2	264.1	5.32	5.29
m-$NH_2C_6H_4$	C_6H_5	89	260–263 dec.	$C_{12}H_{12}NO_2P$	13.28	13.19	233.2	233.3	6.01	6.01
p-$NH_2C_6H_4$	C_6H_5	84	210–211.5	$C_{12}H_{12}NO_2P$	13.28	13.17	233.2	233.4	6.01	6.04
o-BrC_6H_4	C_2H_5	9[c]	98–101	$C_8H_{10}BrO_2P$	12.44	12.66	249.1	250.3		
p-$NO_2C_6H_4$	C_2H_5	15[c]	127–130	$C_8H_{10}NO_4P$	14.40	14.14	215.1	216.8	6.51	6.50
p-$NH_2C_6H_4$	C_2H_5	69	172–173	$C_8H_{12}NO_2P$	16.73	16.65	185.2	183.7	7.57	7.60

[a] Melting points were taken as previously described; *cf.* ref. 1. [b] Phenolphthalein was used as the indicator. [c] These yields were obtained by the use of ethyl acetate as the solvent and cuprous bromide as the catalyst.

100 ml. for preparations on a 0.1 mole scale. The crude phosphinic acid, which crystallized when this solution was cooled, was removed by filtration. The solid was dissolved in 10% sodium hydroxide solution and the solution filtered from a small amount of undissolved material. No phosphine oxide was ever found in this insoluble residue. The alkaline filtrate was treated with Darco, again filtered, and the phosphinic acid reprecipitated by the addition of concentrated hydrochloric acid. The phosphinic acid was finally purified by recrystallization from appropriate solvents.

Diphenylphosphinic acid was readily purified by the recrystallization from aqueous alcohol. The unsymmetrical diarylphosphinic acids were more difficult to purify. Repeated recrystallizations from aqueous alcohol were necessary in order to remove traces of symmetrical diarylphosphinic acids. The arylethylphosphinic acids were even more difficult to obtain in a pure state. Neither aqueous alcohol nor ether were satisfactory recrystallizing solvents. Ethyl acetate proved to be the solvent of choice for the two arylethylphosphinic acids studied.

In two cases symmetrical phosphinic acids were isolated from reactions of ethyldichlorophosphine with diazonium fluoborates. In one experiment 6.2 g. of crude (*p*-nitrophenyl)-ethylphosphinic acid was recrystallized from 50% aqueous alcohol and then extracted with ether in a Soxhlet apparatus for 72 hours. The insoluble residue (0.25 g.) was shown to be bis-(*p*-nitrophenyl)-phosphinic acid by analysis and mixed m.p. with an authentic sample. An attempt to prepare (*m*-nitrophenyl)-ethylphosphinic acid yielded a phosphinic acid, which was recrystallized from 95% alcohol. The recrystallized material was identified as bis-(*m*-nitrophenyl)-phosphinic acid by analysis and mixed m.p. with an authentic sample. It is possible that the desired unsymmetrical acid was formed in small amount, and was lost in the purification process.

Analysis for Phosphorus.—Phosphorus was determined by a modification of the method of Bachofer and Wagner.[6] Details of this modification will be reported elsewhere.

Acknowledgment.—The authors wish to thank Miss Sadie Herndon for performing the analyses necessary for this research and Miss Stella Efland for skilled technical assistance.

(6) M. D. Bachofer and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **15**, 601 (1943).

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Condensation of Saturated Halides with Unsaturated Compounds. VIII. Condensation of Dihaloalkanes with Ethylene and Chloroethylenes[1]

BY LOUIS SCHMERLING AND JAMES P. WEST

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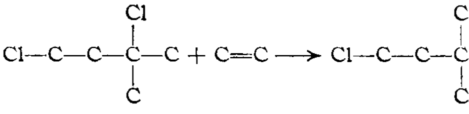
The metal chloride-catalyzed condensation of ethylene and chloroethylenes with dichloroalkanes in which at least one chlorine atom is attached to a tertiary carbon atom results in the formation of polychloroalkanes containing quaternary carbon atoms. For example, the reaction of the readily prepared isoprene dihydrochloride (or the analogous dibromide) with ethylene offers a convenient means for the preparation of 1,5-dihalo-3,3-dimethylpentane, from which a number of heterocyclic compounds with *gem*-dimethyl groups have been synthesized. Two new spiro hydrocarbons, 8,8-dimethylspiro[4,5]-2,4-decadiene and 8,8-dimethylspiro[4.5]decane are described.

In previous papers in this series it was shown that alkyl halides (chlorides and bromides) containing at least three carbon atoms add to olefins[2] and haloölefins[3] in the presence of metal halide catalysts of the Friedel–Crafts type. The present communication describes the extension of the reaction to dihaloälkanes, at least one halogen atom of which is held by a tertiary carbon atom.

The reaction of 1,3-dichloro-3-methylbutane (isoprene dihydrochloride) with ethylene in the presence of aluminum chloride at −12° resulted in a 68% yield of 1,5-dichloro-3,3-dimethylpentane (I). It is apparent that the chlorine atom attached to the tertiary carbon atom is much more reactive than that attached to the primary carbon atom. This finds analogy in the results with the alkyl halides; in general the best yields were obtained with the tertiary alkyl halides and the poorest with the primary isomers.



$$\mathrm{Cl{-}C{-}C{-}\overset{Cl}{\underset{C}{C}}{-}C + C{=}C \longrightarrow Cl{-}C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}Cl}\quad (I)$$

(1) (a) Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951. (b) Preceding paper in this Series, THIS JOURNAL, **71**, 753 (1949).

(2) (a) L. Schmerling, *ibid.*, **67**, 1152 (1945); (b) *ibid.*, **69**, 1121 (1947); (c) L. Schmerling and E. E. Meisinger, *ibid.*, **71**, 753 (1949).

(3) L. Schmerling, *ibid.*, **68**, 1650, 1655 (1946); **71**, 701 (1949).

Under similar conditions, the reaction of the 1,3-dibromo-3-methylbutane with ethylene resulted in a 55% yield of 1,5-dibromo-3,3-dimethylpentane (V).

Condensation of vinyl chloride with the dichloride occurred even more readily. An 84% yield of 1,1,5-trichloro-3,3-dimethylpentane (II) was obtained in the presence of aluminum chloride at −25°. The structure of this product was proved by reducing it to the known[2a] 1-chloro-3,3-dimethylpentane by treatment with zinc and propanol.

When ferric chloride was used as catalyst at 15° for the condensation of the isoprene dihydrochloride with vinyl chloride, a trichloroheptane (III) isomeric with II was obtained in 24% yield together with a 28% yield of a tetrachlorononane; it seems probable that III contained chlorine attached to a secondary or tertiary carbon atom and was therefore sufficiently reactive to condense with vinyl chloride to form the tetrachlorononane. Unlike II, III yields a precipitate when treated with alcoholic silver nitrate.

The reaction of vinylidene chloride with the dichloromethylbutane in the presence of ferric chloride at room temperature resulted in an 18% yield of a tetrachloroheptane (possibly 1,1,1,5-tetrachloro-3,3-dimethylpentane (IV)). Better yields would probably be obtained in the presence of aluminum chloride.

The fact that the condensations are catalyzed by ferric chloride illustrates a significant difference between the present reaction and that of polyhaloalkanes in which two or more halogen atoms are attached to a single carbon atom. Prins[4] has found that the condensation of carbon tetrachloride or chloroform, for example, with chloroölefins is catalyzed only by aluminum chloride and not by ferric chloride or any of the other Friedel–Crafts catalysts. Furthermore, Prins found that the polychloromethanes could be condensed with haloölefins but not with ethylene or other olefins. His observations have been verified in the present investigation.

1,4-Dichloro-2,2-dimethylbutane (VI) and 1,1,4-trichloro-3,3-dimethylbutane (VII), respectively, were produced by the reaction of ethylene and vinyl chloride with 1,2-dichloro-2-methylpropane. Yields were lower than with 1,3-dichloro-3-methylbutane probably because of steric (or related) effects involved in the presence of a chlorine atom on the carbon atom adjacent to the tertiary carbon atom.

2,4-Dichloro-2-methylpentane was investigated as an example of a dihalide in which the chlorine atoms are attached both to a tertiary and a secondary carbon atom. The reaction with ethylene in the presence of aluminum chloride resulted in a 10% yield of the 1:1 condensation product (1,5-dichloro-3,3-dimethylhexane, VIII) and much unidentified higher boiling material, presumably formed by condensation of the dihalide with two or more molecular proportions of ethylene. Similarly, condensation of the dichloromethylpentane with vinyl chloride resulted in a 48% yield of 1,1,5-trichloro-3,3-dimethylhexane (IX) and a 24% yield of tetrachlorodecane (IXA). The latter was probably 1,1,7,7-tetrachloro-3,3,5-trimethylheptane formed by condensations at both the tertiary and the secondary carbon atoms holding the chlorine atoms; alternatively, skeletal rearrangement of IX to 1,1,3-(or 4)-trichloro-3,4-dimethylhexane may have preceded the reaction with the second molecule of ethylene to yield 1,1-dichloro-3-(2,2-dichloroethyl)-3,4-dimethylhexane (compare the analogous intermediate rearrangement of neopentyl chloride to *t*-pentyl chloride during the reaction with ethylene[1b]).

The reaction of vinyl chloride with 2,5-dichloro-2,5-dimethylhexane, a dichloroalkane in which both chlorine atoms are attached to tertiary carbon atoms, involved two molecular proportions of the unsaturated chloride. The major reaction product (45% yield) was 1,1,8,8-tetrachloro-3,3,6,6-tetramethyloctane (X).

The 1,5-dihalo-3,3-dimethylpentanes (I and V) obtained by the reaction of ethylene with the 1,3-dihalo-3-methylbutanes (which are readily prepared by the addition of the hydrogen halides to isoprene) offer a practical and convenient means for the synthesis of a number of cyclic compounds containing *gem*-dimethyl groups. A few examples will be described.

4,4-Dimethyltetrahydropyran was obtained by the reaction of the 1,5-dichloro-3,3-dimethylpentane with a dilute aqueous solution of magnesium hydroxide at 210°. When a solution of sodium sulfide was used under similar conditions, 4,4-dimethyltetrahydrothiopyran was produced.

The reaction of the dichloride with ammonium hydroxide at 210° gave a fair yield of 4,4-dimethylpiperidine. The major product was the crystalline spiro-nitrogen compound, 4,4,9,9-tetramethylbispiperidinium chloride, formed by the reaction of the dichlorodimethylpentane with the dimethylpiperidine. The analogous 4,4-dimethylbispiperidinium chloride was prepared by heating the dichlorodimethylpentane with piperidine.

Ring closure with the formation of N-substituted piperidines proceeded smoothly when the 1,5-dichloro- or 1,5-bromo-3,3-dimethylpentane was treated with a primary amine. 1-Isopropyl-4,4-dimethylpiperidine, 1-phenyl-4,4-dimethylpiperidine and 1,4-bis-(4,4-dimethylpiperidino)-benzene were synthesized by the reaction of the dihalide with isopropylamine, aniline and *p*-phenylenediamine, respectively.

A new spirohydrocarbon, 8,8-dimethylspiro[4.5]-2,4-decadiene, was prepared by the reaction of 1,5-dibromo-3,3-dimethylpentane with cyclopentadiene and sodium in liquid ammonia. Hydrogenation of the diene yielded 8,8-dimethylspiro[4.5]decane.

Experimental[5]

Materials.—The ethylene (The Ohio Chemical and Manufacturing Company) and the chloroethylenes (The Dow Chemical Company) were the commercially available products. The dihaloalkanes were prepared by the addition of a hydrogen halide to a diene or a chloroölefin at super-atmospheric pressure. Yields were higher than those previously reported for reactions carried out at atmospheric pressure,

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[4] H. J. Prins, *Rec. trav. chim.*, **51**, 1065 (1932).

[5] Microanalyses by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

TABLE I

CONDENSATION OF DIHALOALKANES WITH ETHYLENE AND CHLOROETHYLENES

Method	Reactants			Catalyst		Temp., °C.	Duration, hr.	Chief product			Higher boiling prod., g.
	RX_2, g.	Unsatd.	Compound G	MX_3	G.			Compound	G.	%	
1,3-Dichloro-3-methylbutane											
A	252	C_2H_4	62[a]	$AlCl_3$	15[b]	−15 to −10	4.0	I	205	68	40
A	66	C_2H_3Cl	40	$AlCl_3$	2	−30 to −20	0.8	II	80	84	14
T	50	C_2H_3Cl	25	$AlCl_3$	1	−48 to +10[c]	...	II	31	43[d]	7
T	50	C_2H_3Cl	25	$FeCl_3$	2	5 to 20	1.5	III	16	24	
								IIIA	15	28[e]	5
T	33	CH_2CCl_2	22	$FeCl_3$	1	15 to 30	1.0	IV	10	18	5
1,3-Dibromo-3-methylbutane											
A	200	C_2H_4	23[a]	$AlCl_3$	6	−15 to −10	1.5	V	129	55	15
1,2-Dichloro-2-methylpropane											
A	50	C_2H_4	5[a]	$AlCl_3$	4[f]	10 to 20	0.8	VI	13	21	7
T	9	C_2H_3Cl	14	$AlCl_3$	1	−25 to +24	0.1	VII	6	45	1
2,4-Dichloro-2-methylpentane											
A	115	C_2H_4	6[a]	$AlCl_3$	11[b]	0 to 8	1.8	VIII	14	10	25
A	150	C_2H_3Cl	70	$AlCl_3$	5	−15 to 0	1.0	IX	100	48	
								IXA	28	24[e]	11
2,5-Dichloro-2,5-dimethylhexane											
T	8	C_2H_3Cl	18	$AlCl_3$	1	8 to 22	2.0	X	6	45	4

[a] As measured by increase in weight of reaction mixture. [b] Added in three portions. [c] The mixture of reactants and catalyst was gradually warmed from −78°. A sudden reaction occurred at about −48° and the temperature reached +10° in thirty seconds even though the reaction tube was quickly immersed in the bath at −78°. About one-third of the mixture was blown from the tube. [d] Yield on a no loss basis, 65%. [e] Based on the vinyl chloride. [f] Added in two portions.

TABLE II

PROPERTIES OF THE CONDENSATION PRODUCTS

No.	Formula	B.p.		B.p. at 760 mm., °C.[a]	$n^{20}D$	d^{20}_4	Mol. ref.		Analyses,[b] %					
									Calcd.			Found		
		°C.	Mm.				Calcd.	Obsd.	C	H	X	C	H	X
I	$ClCH_2CH_2CMe_2CH_2CH_2Cl$[c]	75–76	3	218–229	1.4652	1.0563	44.2	44.1	49.70	8.34	41.96	49.82	8.36	41.03
II	$ClCH_2CH_2CMe_2CH_2CHCl_2$	90–91	4	239–240	1.4805	1.1780	49.2	49.1	41.30	6.44	52.26	41.43	6.62	51.71
III	$C_7H_{13}Cl_3$	83–84	3.5	230–231	1.4715	1.1558	49.2	49.0	41.30	6.44	52.26	40.90	6.38	52.36
IIIA	$C_9H_{16}Cl_4$	131–132	4	298–299	1.4892	1.2103	63.3	63.4	40.60	6.07	53.33	41.10	6.20	52.81
IV	$C_7H_{12}Cl_4$	91–92	3	241–242	1.4800	1.2343	54.1	54.6	35.31	5.08	59.61	35.68	5.22	59.25
V	$BrCH_2CH_2CMe_2CH_2CH_2Br$	98–99	3	254–255	1.5091	1.5287	50.1	50.4	32.57	5.47	61.96	32.68	5.50	60.25
VI	$ClCH_2CMe_2CH_2CH_2Cl$	78–80	20	182–185	1.4594	1.0683	39.6	39.7	46.50	7.75	45.75			
VII	$ClCH_2CMe_2CH_2CHCl_2$	70–70	4	210–210	1.4761	1.2082	44.5	44.2	38.00	5.85	56.15	37.69	5.87	
VIII	$CH_3CHClCH_2CMe_2CH_2CH_2Cl$	78–84	3	225–234	1.4643	1.0193	48.8	49.3	52.45	8.81	38.74	54.12	9.14	36.48
IX	$CH_3CHClCH_2CMe_2CH_2CHCl_2$	84–88	2	242–248	1.4809	1.1608	53.7	53.3	44.14	6.95	48.91	44.16	7.01	47.75
IXA	$C_{10}H_{18}Cl_4$	126–128	2	300–303	1.4930	1.2033	67.9	67.6	42.87	6.48	50.65	43.34	6.70	49.82
X	$C_{12}H_{22}Cl_4$[d]	151–152	3	321–322	1.4895	1.1564	77.1	77.0	46.75	7.20	46.05	47.20	7.20	45.67

[a] Calculated from boiling under reduced pressure using Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946). [b] Microanalyses by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois. [c] G. Komppa, *Ber.*, **62**, 1371 (1929); R. F. Miller and R. Adams, THIS JOURNAL, **58**, 787 (1936). [d] $Cl_2CHCH_2CMe_2CH_2CH_2CMe_2CH_2CHCl_2$.

which in many cases yield chiefly chloroölefins by the reaction of hydrogen chloride with the dienes.

1,3-Dichloro-3-methylbutane[6] was obtained in 86% yield by the reaction of isoprene and hydrogen chloride under 30 atm. initial pressure at room temperature; b.p. 60° (30 mm.) $n^{20}D$ 1.4465, d^{20}_4 1.0758; MR_D calcd. 35.00, obsd. 34.96.

1,3-Dibromo-3-methylbutane[7] was prepared in 82% yield in analogous manner by the reaction of hydrogen bromide with isoprene; b.p. 54–55° (4 mm.); $n^{20}D$ 1.5065.

1,2-Dichloro-2-methylpropane[8] was prepared by adding hydrogen chloride to methallyl chloride; 83% yield; b.p. 105–106°; $n^{20}D$ 1.4378.

2,4-Dichloro-2-methylpentane was synthesized by the hydrochlorination of 2-methylpentadiene (b.p. 73–74.5°, largely 2-methyl-1,3-pentadiene); yield 65%; b.p. 70–71° (48 mm.), $n^{20}D$ 1.4435, d^{20}_4 1.0360; MR_D calcd. 39.60, obsd. 39.65.

2,5-Dichloro-2,5-dimethylhexane[9] was obtained in 87% yield by saturating a solution of 2,5-dimethyl-1,5-hexadiene (prepared by the action of magnesium on methallyl chloride in dry ether; b.p. 112–113°; $n^{20}D$ 1.4291) in acetic acid with anhydrous hydrogen chloride at 0°; white crystals, m.p. 65°.

Procedures.—The experimental procedures will be summarized very briefly since they were similar to those previously described for the reaction of alkyl halides with ethylene[2] and with chloroethylene.[3]

In method A, ethylene or vinyl chloride was bubbled into a stirred mixture of the dihaloalkane and the catalyst. When ethylene was used, the temperature of the mixture was permitted to rise slowly from about −60° to the temperature at which the absorption of the olefin began (as indicated by the difference in rate of bubbling in an inlet and exit bubbler) and was then maintained at about that point for the duration of the experiment.

In method T, the mixture of reactants and catalyst in a large test-tube was shaken manually while the temperature rose gradually from −60° to the temperature of incipient

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[6] G. Bouchardat, *Compt. rend.*, **89**, 1118 (1879). I. Kondakov, *J. Russ. Phys. Chem. Soc.*, **29**, 1513 (1892).

[7] V. N. Ipatieff, *J. prakt. Chem.*, [2] **55**, 4 (1897).

[8] J. Burgin, W. Engs, H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

[9] Z. A. Pogorshelsky, *J. Russ. Phys. Chem. Soc.*, **30**, 977 (1898); *Chem. Zentr.*, **70**, I, 773 (1899).

reaction, indicated by the evolution of tiny bubbles of gas. The test-tube was intermittently cooled and warmed until there was little sign of reaction at a temperature at least 10° higher than the original reaction temperature. This method, which was admittedly crude and was not expected to give the highest possible yields of product, had the advantage that the experiments could be carried out quickly.

Conversion of 1,1,5-Trichloro-3,3-dimethylpentane (II) to 1-Chloro-3,3-dimethylpentane.—A solution of 6 g. of II in 25 cc. of propanol was heated under reflux with 9 g. of 80-mesh zinc granules for 15 hours. Water was then added and the product was distilled. There was obtained 2.5 g. of water-insoluble material which was combined with the liquid product obtained from a similar experiment using 8 g. of the trichloride and fractionated through a Piros–Glover microfractionation column. There was obtained 2 g. of 1-chloro-3,3-dimethylpentane boiling at 65° at 47 mm. (145° at 760 mm.); n^{20}_{D} 1.4302. There was also recovered about 6 g. of unreacted trichloride. The product boiling at 65° (47 mm.) was shown to be chiefly 1-chloro-3,3-dimethylpentane by comparing its infrared spectrum[10] with that of the material obtained by the condensation of ethylene with *t*-pentyl chloride[2a] or neopentyl chloride.[1b]

Derivatives of 1,5-Dihalo-3,3-dimethylpentane. 4,4-Dimethyltetrahydropyran.—A sealed tube containing 13.5 g. (0.08 mole) of 1,5-dichloro-3,3-dimethylpentane (I) 5 g. (0.12 mole) of magnesium oxide and 100 g. of water was heated at 250° for four hours in a rotating autoclave. Water was placed in the autoclave outside the tube in order to nearly equalize the pressure and prevent breakage. Steam distillation of the product followed by redistillation of the upper layer material yielded 7.5 g. (82%) of dimethyltetrahydropyran, b.p. 124–125°; n^{20}_{D} 1.4239.

Anal. Calcd. for $C_7H_{14}O$: C, 73.62; H, 12.36. Found: C, 73.45; H, 12.35.

4,4-Dimethyltetrahydrothiopyran.—The reaction of 15 g. (0.09 mole) of I and a solution of 40 g. (0.17 mole) of sodium sulfide nonahydrate in 100 g. of water at 210° for four hours yielded 8.5 g. (73%) of the dimethyltetrahydrothiopyran, b.p. 57–58° (13 mm.), n^{20}_{D} 1.4900.

Anal. Calcd. for $C_7H_{14}S$: C, 64.56; H, 10.84; S, 24.60. Found: C, 64.89; H, 10.95; S, 24.65.

4,4-Dimethylpiperidine.—A mixture of 15 g. (0.09 mole) of I and 56 cc. (1.1 moles) of concentrated ammonium hydroxide was heated at 210° for four hours in a sealed tube. The product was a mixture of nacreous crystals and aqueous solution. It was made alkaline with sodium hydroxide and steam distilled. The upper layer of the distillate (5 g., 49% yield) was dried and redistilled. It boiled at 135–138°, n^{20}_{D} 1.4470; phenylthiourethan, m.p. 136°. Komppa[11] prepared 4,4-dimethylpiperidine by the reduction of β,β-dimethylglutarimide with sodium and alcohol; b.p. 145–146°; phenylthiourethan, m.p. 136°.

The residue from the steam distillation yielded crystals (nacreous flakes, 3 g., 27%) when cooled; m.p. above 300°. The compound contained ionizable chlorine as indicated by the reaction with aqueous silver nitrate. The chlorine could not, however, be replaced by hydroxyl by reaction with alkali. These properties indicate that the product was 4,4,9,9-tetramethylbispiperidinium chloride.

A second experiment was carried out in the presence of a smaller proportion of ammonia in order to obtain a larger yield of the piperidinium chloride. A sealed tube containing 30 g. (0.18 mole) of I, 8 g. (0.2 mole) of magnesium oxide, 25 g. (0.5 mole of ammonia) of concentrated ammonium hydroxide, and 70 g. of water was heated at 210° for four hours. The product was steam distilled to remove a small amount (3 g., 15%) of the dimethylpiperidine. Filtration of the cooled residue yielded 11 g. of white crystals of the tetramethylbispiperidinium chloride; concentration of the filtrate produced an additional 3 g. of the material (total yield 63%).

4,4-Dimethylbispiperidinium Chloride.[12]—A mixture of 11 g. (0.13 mole) of piperidine and 5.5 g. (0.03 mole) of I was heated to 110° under a reflux column. The clear solution rapidly turned turbid and a thick mass of crystals separated in about 10 minutes. Attempts to reflux the mixture were unsuccessful; charring occurred when the mixture was heated to 175°. The product was cooled, water was added and the mixture was steam distilled. About 2 cc. of water-insoluble distillate (denser than water) was obtained. The residue in the flask deposited crystals when cooled. Filtration yielded 5.5 g. (80%) of fine soft needles which were very soluble in water. More of the product was probably present in the filtrate.

1-Isopropyl-4,4-dimethylpiperidine.—The product of the reaction of 12 g. (0.20 mole) of isopropylamine, 17 g. (0.10 mole) of I and 5 g. (0.12 mole) of magnesium oxide in 50 g. of water at 200° was steam distilled to obtain 16 cc. of organic distillate which was dried and redistilled, yield 10 g. or 65%; b.p. 72–74° (19 mm.), n^{20}_{D} 1.4461.

Anal. Calcd. for $C_{10}H_{21}N$: C, 77.34; H, 13.64; N, 9.02. Found: C, 77.47; H, 13.47; N, 9.18.

1-Phenyl-4,4-dimethylpiperidine.—A solution of 22 g. (0.09 mole) of 1,5-dibromo-3,3-dimethylpentane (V) and 30 g. (0.32 mole) of aniline and 50 cc. of methylcyclohexane was heated under reflux (108°) for eight hours. A white salt separated. Water was added and the mixture was distilled to remove about 6 cc. of water-insoluble material. The residue in the distilling flask was cooled, extracted with ether and the extract washed, dried and distilled. 1-Phenyl-4,4-dimethylpiperidine, b.p. 117–118° (3 mm.), n^{20}_{D} 1.5434, was obtained in 30% yield.

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.54; H, 9.90; N, 7.65.

1,4-Bis-(4,4-dimethylpiperidino)-benzene.—A solution of 5.4 g. (0.05 mole) of *p*-phenylenediamine and 26 g. (0.01 mole) of V in 50 cc. of methylcyclohexane and 25 cc. of *n*-propyl alcohol was refluxed at 87° in the presence of 14 g. (0.1 mole) of anhydrous potassium carbonate for 16 hours. The solvent was distilled off, water was added to the residue and the mixture was steam distilled. There was obtained in the distillate 5 cc. of upper layer and 30 cc. of water. The product in the flask crystallized on cooling. The violet crystals were filtered and recrystallized from alcohol. There was obtained 5.5 g. (37%) of nacreous flakes having a purplish tint; m.p. 168°. A second recrystallization from alcohol yielded pink flakes, m.p. 168°.

Anal. Calcd. for $C_{20}H_{32}N_2$: C, 79.93; H, 10.74; N, 9.33. Found: C, 80.33; H, 10.48; N, 9.47.

8,8-Dimethylspiro[4.5]-2,4-decadiene.—Cyclopentadiene (7 g., 0.11 mole) was added to a stirred solution of 5 g. (0.21 mole) of sodium in 67 cc. of absolute alcohol at 2°. A brown precipitate separated. Twenty-five grams (0.10 mole) of V was added and the stirred mixture was heated to 60°. A white salt precipitated. The temperature was maintained at 60–70° for two hours, the mixture was then cooled, water was added and the product was steam distilled. There was obtained 9 cc. of organic distillate which was taken up in ether and distilled. The major portion of the material (4 g., 23%) boiled at 43–50° (2 mm.); n^{20}_{D} 1.4808.

The spirodecadiene was also prepared by carrying out the reaction in liquid ammonia. Cyclopentadiene (18 g., 0.27 mole) was added to a solution of 10 g. (0.42 mole) of sodium in 120 g. of liquid ammonia. Fifty-two grams (0.20 mole) of V was then added dropwise with stirring during one-half hour. The blue color of the solution disappeared after about two-thirds of the dibromide had been added. The solution was stirred for an additional one-half hour, water was added and the organic product was taken up in ether, washed, dried and distilled. There was obtained 6.5 g. (20%) of material boiling at 52–54° (2.5 mm.), n^{20}_{D} 1.4810.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.83; H, 11.17. Found: C, 86.77; H, 10.86. Reaction of the diene with air is indicated.

The maleic anhydride adduct of the spirodecadiene was prepared; m.p. 140°.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.80; H, 7.75. Found: C, 74.31; H, 7.83.

8,8-Dimethylspiro[4.5]decane.—The batches of dimethylspirodecadiene prepared in the two experiments described above were combined and the resulting 10.6 cc. of material was dissolved in 11 cc. of *n*-pentane and hydrogenated at 50–75° in the presence of UOP nickel–kieselguhr. The

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(10) Infrared absorption analysis by Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company.

(11) G. Komppa, *C. A.*, **7**, 1359 (1913).

(12) *Cf.* J. v. Braun, *Ber.*, **39**, 4347 (1906), who prepared bispiperidinium bromide by the reaction of 1,5-dibromopentane with piperidine in chloroform solution.

major portion of the hydrogenated material boiled at 57–58° (2 mm.) or 208–209° (760 mm.); n^{20}_{D} 1.4668. Its melting point was about −22° as determined with a thermometer immersed in the mixture of liquid and crystals.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.65; H, 13.35. Found: C, 86.79; H, 13.11.

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING]

Further Studies of Anomalous Alkylations with β-Dialkylaminoethyl Chlorides

BY SARA JANE RHOADS, ROSALIE D. REYNOLDS AND REBECCA RAULINS

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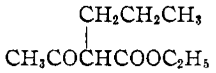
The alkylations of the cyclic β-ketoesters, 2-carbethoxycyclohexanone and 2-carbethoxycyclopentanone with β-dimethylaminoethyl chloride and β-diethylaminoethyl chloride give rise to mixtures of C- and O-alkylated products under a variety of conditions. The open chain analog, ethyl α-acetylvalerate, undergoes C-alkylation exclusively with β-dimethylaminoethyl chloride.

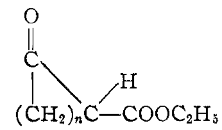
The appearance in the recent literature[1a,b,c] of several examples of anomalous O-alkylation of active carbonyl compounds by β-dialkylaminoethyl halides and structurally similar compounds[2] has prompted an investigation of the extent of the abnormal reaction as influenced by the following factors: structure of the carbonyl compound[3] (*i.e.*, degree of substitution at the α-carbon, ring *vs.* open chain structure), solvent and temperature. The influence of solvent has been demonstrated in one case[1a]; the use of a non-polar solvent appears to favor C-alkylation. A temperature dependence in situations of this general type which involve competitive reactions of a mesomeric anion has been predicted by Dewar.[4]

In this investigation, three β-ketoesters, ethyl α-acetylvalerate (I), 2-carbethoxycyclohexanone (IIa) and 2-carbethoxycyclopentanone (IIb) have been studied under a variety of conditions. The results are summarized in Table I.



$CH_3CO\overset{\overset{CH_2CH_2CH_3}{|}}{C}HCOOC_2H_5$

I



IIa, *n* = 4
IIb, *n* = 3

With β-dimethylaminoethyl chloride (IIIa) the potassio-derivative of I in refluxing *t*-butyl alcohol reacts to give only the normal C-alkylated product, IV (Expt. 1). Acid hydrolysis and decarboxylation of the alkylated product proceed without loss of basicity to yield 1-dimethylamino-3-propylpentanone-4 (V) in good yield. Under these same conditions the cyclic anlog IIa has been observed to give mainly the O-alkylated product VIa (Expt. 2).

TABLE I

Expt. no.	β-Keto-ester	Alkylating reagent	Conditions: base, solvent temp. and time	Alkylated Total yield, %	Products Composition	
					C, %	O, %
1	I	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 3 hours	49	100[a]	0
2[b]	IIa	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 6 hours	60	19	72
3	IIa	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, room temp., 67 hours	40	26	66
4[b]	IIa	IIIa	Sodium sand, toluene, reflux, 6 hours	42[c]	42	42
5	IIa	IIIa	Sodium *t*-butoxide, *t*-butyl alcohol, reflux, 6 hours	70	22	68
6	IIa	IIIb	Sodium sand, toluene, reflux, 6 hours	71	34[d]	51[d]
7	IIb	IIIb	Sodium hydride, benzene, reflux, 6 hours	50	24	61
8	IIb	IIIb	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 3 hours	63	22	62
9	IIb	IIIb	Potassium *t*-butoxide, *t*-butyl alcohol, room temp., 4 hours	71	22	56

[a] Percentage is based on the fact that no O-derivative could be detected. [b] Data taken from ref. 1a. [c] On repetition, this yield has been materially improved (63%); the composition of the product remains the same, however: 42% O-; 42% C-. [d] Duplicate determinations gave results in agreement within 1.5% and provide a reasonable indication of the probable error in the other percentages reported.

Barltrop[5] reported the sodio-derivative of IIa to give the normal C-alkylated product when treated with β-diethylaminoethyl chloride in refluxing toluene. Repetition of this work has shown that the alkylation product is actually a mixture of C- (VIIb) and O-alkylated (VIb) derivatives, the abnormal product predominating (Expt. 6).

With β-diethylaminoethyl chloride (IIIb), the sodio- or potassio-enolate of 2-carbethoxycyclopentanone (IIb), is alkylated rapidly in benzene or

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(1) (a) W. von E. Doering and S. J. Rhoads, THIS JOURNAL, **73**, 3082 (1951); (b) J. C. Sheehan and C. E. Mumaw, *ibid.*, **72**, 2127 (1950); (c) N. Sperber, R. Fricano and D. Papa, *ibid.*, **72**, 3068 (1950).

(2) See the sources cited and references there for other examples.

(3) Although the anomalous alkylation has been observed most frequently with halides of unusual reactivity, evidence that the nature of the alkylating agent is not the sole cause of the anomaly is derived from the fact that certain cyclic compounds such as 2-cyanocyclohexanone [K. von Auwers, *Ber.*, **61**, 408 (1928)] and 2-carbethoxy-5-cyanocyclopentanone [S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 685 (1909)] have been reported to undergo both C- and O-alkylation under normal alkylating conditions even with the relatively unreactive alkyl halides. *Cf.*, also, the exclusive C-alkylation experienced with the open chain acetoacetic ester (ref. 1a and footnote 8 of that reference) and β-dialkylaminoethyl chlorides.

(4) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford at the Clarendon Press, 1949, p. 104.

(5) J. A. Barltrop, *J. Chem. Soc.*, 399 (1947).