hr. Evaporation of the solvent and trituration of the residue with water yielded crude phthalazone (XII, 75 mg, 52%) which, after recrystallization from methanol-ether-hexane, melted at 182° and was identical by infrared comparison with an authentic sample.

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Photochlorination of 2,4-Dimethylpentane, 2,2,4-Trimethylpentane, and 2,2,4,4-Tetramethylpentane[1]

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The methine hydrogens of 2,4-dimethylpentane and 2,2,4-trimethylpentane possess unusually low reactivity toward the free or complexed chlorine atom. This result has been explained in terms of conformational effects in the hydrocarbons that shield the methine hydrogen atoms from radical attack.

The low reactivity of the tertiary hydrogen atom of 2,2,4-trimethylpentane (isooctane) in autoxidation has been deduced from rate and product studies,[2] and in the attack of methyl radicals by product isolation.[3] The over-all abnormally low reactivity of 2,4-dimethylpentane and isooctane toward *t*-butoxy[4] and phenyl radicals[5] has been interpreted in terms of conformational effects which essentially shield the tertiary hydrogen atoms from attack by radical species. The present results on over-all reactivity and substitution products in photochlorination support this conclusion. These results also provide additional examples of specific solvent effects in the reaction of chlorine atoms with carbon hydrogen bonds.[6]

Results

2,4-Dimethylpentane.—Photochlorination of 99 mole % minimum 2,4-dimethylpentane in carbon tetrachloride, 4 *M* benzene, or 12 *M* carbon disulfide with 5 mole % of chlorine at 40°[7] produced three monochlorides that could be separated by gas-liquid partition chromatography (glpc) at 50° on a 100 m × $^1/_{16}$ in. i.d. copper Golay column coated with polypropylene glycol. The relative retention times were 1:1.16:1.25. The chloride with the lowest retention time was 2-chloro-2,4-dimethylpentane as ascertained by comparison with the retention time of the tertiary chloride produced by treatment of 2,4-dimethyl-2-pentanol with hydrogen chloride at room temperature. The chloride with the longest retention time was the primary chloride, 1-chloro-2,4-dimethylpentane, since the same chloride was produced by treatment of 2,4-dimethyl-1-pentanol with thionyl chloride. The chloride with the intermediate retention time was assigned to the secondary chloride, 3-chloro-2,4-dimethylpentane. The composition of the monochlorides produced is summarized in Table I and average yields listed in Chart I.

TABLE I

COMPOSITION OF MONOCHLORIDES FORMED IN CHLORINATION OF METHYLPENTANES AT 40°

Solvent	Chlorides (% of total monochlorides)		
	Primary	Secondary	Tertiary
	2,4-Dimethylpentane		
CCl_4[a]	55.1	22.9	22.0
	55.5	23.0	21.5
	54.3	23.2	22.5
4 *M* C_6H_6[a]	33.5	30.2	36.3
	33.4	30.6	36.0
	33.1	30.9	36.0
12 *M* CS_2[b]	10.5	35.8	53.7
	11.1	35.2	53.7
	12.3	36.5	51.2
	9.6	35.0	55.4
	2,2,4-Trimethylpentane		
CCl_4[a]	70.6	24.6	4.8
	70.6	24.6	4.8
	70.2	24.4	5.4
	70.1	24.4	5.5
	67.4	26.0	6.6
	67.4	26.0	6.6
4 *M* C_6H_6[a]	50.5	39.7	9.8
	49.5	40.9	9.6
	51.1	40.1	8.8
12 *M* CS_2[b]	19.3	59.8	20.9
	20.7	57.1	22.2
	20.8	55.8	23.4
	22.6	51.5	25.9
	22.1	53.0	24.9
	2,2,4,4-Tetramethylpentane		
CCl_4[a]	81.8	18.2	
	82.6	17.4	
	81.1	18.9	
4 *M* C_6H_6[a]	52.5	47.6	
	52.0	48.0	
	51.5	48.5	

[a] *Ca.* 5 mole % chlorination. [b] *Ca.* 2 mole % chlorination.

Competitive chlorinations with cyclohexane were performed in carbon tetrachloride, benzene, and carbon disulfide solutions. The relative reactivities of cyclohexane and 2,4-dimethylpentane summarized in Table II are based on the rates of disappearance of the two hydrocarbons as measured by glpc.

2,2,4-Trimethylpentane.—Photochlorination of 99 mole % minimum 2,2,4-trimethylpentane produced four monochlorides, which at 50° on a polypropylene glycol column had relative retention times of 1:1.09:

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(1) Directive Effects in Aliphatic Substitutions. XXIX. For part XXVIII, see G. A. Russell and Y. R. Vinson, *J. Org. Chem.*, **31**, 1994 (1966).

(2) J. P. Wibaut and A. Strang, *Koninkl. Ned. Akad. Wetenschap, Proc.*, **B54**, 229 (1951); C. E. Frank and A. V. Blackham, *Ind. Eng. Chem.*, **46**, 212 (1954); F. F. Rust and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954).

(3) A. L. J. Beckwith, *J. Chem. Soc.*, 2248 (1962).

(4) J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957).

(5) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(6) G. A. Russell, *ibid.*, **80**, 4987, 4997, 5002 (1958).

(7) For experimental details of the technique, see G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).

CHART I

		Yield, % of total		
		CCl_4	4 *M* C_6H_6	12 *M* CS_2
$(CH_3)_2CHCH_2CH(CH_3)_2$	$\rightarrow (CH_3)_2CHCH_2CH(CH_3)CH_2Cl$	55.0	33.3	10.8
	$\rightarrow (CH_3)_2CHCHClCH(CH_3)_2$	23.0	30.6	35.6
	$\rightarrow (CH_3)_2CHCH_2C(CH_3)_2Cl$	22.0	36.1	53.6

CHART II

		Yield, % of total		
		CCl_4	4 *M* C_6H_6	12 *M* CS_2
$(CH_3)_3CCH_2CH(CH_3)_2$	$\rightarrow \left\{\begin{matrix}(CH_3)_3CCH_2CH(CH_3)CH_2Cl \\ (CH_3)_2CHCH_2C(CH_3)_2CH_2Cl\end{matrix}\right\}$	69.4	50.4	21.0
	$\rightarrow (CH_3)_3CCHClCH(CH_3)_2$	25.0	40.2	55.5
	$\rightarrow (CH_3)_3CCH_2C(CH_3)_2Cl$	5.6	9.4	23.5

TABLE II

COMPETITIVE PHOTOCHLORINATION OF METHYLPENTANES WITH CYCLOHEXANE AT 40°

	Pentane, *M*		Cyclohexane, *M*		$k_{\text{pentane}}{}^a / k_{\text{cyclohexane}}$
Solvent	Initial	Final	Initial	Final	
	2,4-Dimethylpentane				
CCl_4	0.970	0.825	1.006	0.804	0.72
	0.970	0.811	1.006	0.792	0.74
	1.00	0.874	1.00	0.834	0.74
	1.00	0.825	1.00	0.771	0.74
	1.00	0.816	1.00	0.757	0.73
	1.00	0.827	1.00	0.779	0.76
4 *M* C_6H_6	2.30	1.96	2.74	2.16	0.67
	2.30	2.16	2.74	2.50	0.69
	2.30	2.18	2.74	2.52	0.64
	2.30	2.14	2.74	2.49	0.75
12 *M* CS_2	1.00	0.909	1.008	0.860	0.61
	1.00	0.916	1.008	0.868	0.59
	1.00	0.856	1.00	0.791	0.66
	1.00	0.860	1.00	0.789	0.64
	1.00	0.840	1.00	0.755	0.62
	2,2,4-Trimethylpentane				
CCl_4	1.00	0.865	1.07	0.899	0.83
	1.00	0.860	1.07	0.881	0.77
	1.00	0.862	1.07	0.875	0.73
	1.10	0.919	1.12	0.887	0.78
4 *M* C_6H_6	1.62	0.959	3.41	1.54	0.66
	1.62	0.880	3.41	1.43	0.70
12 *M* CS_2	1.00	0.796	1.00	0.922	0.32
	1.00	0.820	1.00	0.936	0.43
	1.00	0.734	1.00	0.896	0.36
	1.00	0.850	1.00	0.937	0.40
	2,2,4,4-Tetramethylpentane				
CCl_4	0.452	0.409	0.456	0.387	0.63
	0.452	0.381	0.456	0.344	0.61
4 M C_6H_6	0.608	0.565	0.608	0.474	0.29
	0.608	0.518	0.608	0.362	0.31

[a] Calculated by the expression, $k_{\text{pentane}}/k_{\text{cyclohexane}}$ = log ([pentane]$_f$/[pentane]$_i$)/log ([cyclohexane]$_f$/[cyclohexane]$_i$).

1.15:1.18. The two chlorides with the longer retention times were not completely resolved and were present in a ratio very close to 2:3 with the chloride having the longest retention time in excess. These were assigned to 1-chloro-2,4,4-trimethylpentane (two parts) and 1-chloro-2,2,4-trimethylpentane (three parts). Authentic 1-chloro-2,4,4-trimethylpentane, prepared from 2,4,4-trimethylpentene by hydroboration and subsequent oxidation to the primary alcohol and conversion to the primary chloride by thionyl chloride, had an identical retention time with the third peak observed in the glpc. The lowest retention time was assigned to the tertiary chloride, 2-chloro-2,4,4-trimethylpentane, since the tertiary chloride formed by addition of hydrogen chloride to 2,4,4-trimethylpentene at 0° had an identical retention time. The second peak in glpc was assigned to the secondary chloride, 3-chloro-2,2,4-trimethylpentane. Results of photochlorination (~5 mole % chlorine) in various solvents are listed in Table I and summarized in Chart II.

Competitive photochlorinations with cyclohexane are summarized in Table II.

2,2,4,4-Tetramethylpentane.—Photochlorination of a National Bureau of Standards sample of 99.9 mole % 2,2,4,4-tetramethylpentane produced only two monochlorides separable by glpc at 50° with a 100-m Golay column of polypropylene glycol. The lower retention time was assigned to the secondary chloride. Upon photochlorination in carbon tetrachloride solution, the glpc peak assigned to the primary chloride was somewhat more than four times as large as the peak assigned to the secondary chloride. This assignment is reasonable since the primary chloride is expected to be the predominant chlorinated species in carbon tetrachloride solution. There are nine primary hydrogens per secondary hydrogen atom and for many alkanes $k_{\text{sec-H}}/k_{\text{prim-H}}$ is ~2.5. Results of the chlorinations are listed in Tables I and II and are summarized in Chart III.

Discussion

The "normal" relative reactivity of a primary alkyl hydrogen atom relative to a cyclohexane hydrogen atom at 40° is 0.35–0.45 in aliphatic solvents or in the vapor phase.[7] This relative reactivity for the "normal" hydrocarbon, 2,3-dimethylbutane, decreases to 0.20 in 4 *M* benzene and to ~0.05 in 12 *M* carbon disulfide.[6] That the primary hydrogen atoms of 2,4-dimethyl- and 2,2,4-trimethylpentane have normal reactivities is apparent from an inspection of the data of Table III.

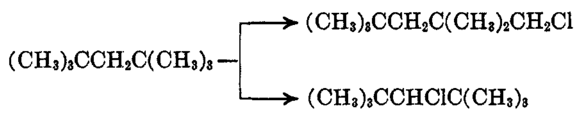
TABLE III

REACTIVITIES OF PRIMARY HYDROGEN ATOMS RELATIVE TO A CYCLOHEXANE HYDROGEN ATOM AT 40°

	Solvent		
Hydrocarbon	CCl_4	4 *M* C_6H_6	12 *M* CS_2
"Normal"	0.35–0.45	0.20	0.05
2,4-Dimethylpentane	0.41	0.23	0.067
2,2,4-Trimethylpentane	0.44	0.27	0.064
2,2,4,4-Tetramethylpentane	0.34	0.11	. . .

It is, therefore, permissible to discuss the reactivities of secondary and tertiary hydrogen atoms relative to

CHART III



$(CH_3)_3CCH_2C(CH_3)_3$

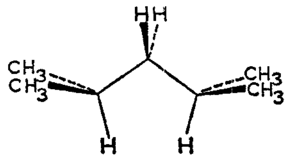
	Yield, % of total	
	CCl_4	4 *M* C_6H_6
$\rightarrow (CH_3)_3CCH_2C(CH_3)_2CH_2Cl$	81.8	52
$\rightarrow (CH_3)_3CCHClC(CH_3)_3$	18.2	48

primary hydrogen atoms within the methylpentanes and to compare these reactivities with "normal" reactivities. At 40° in an aliphatic liquid phase a "normal" tertiary to primary relative reactivity is *ca.* 4.[6] This value increases to 16 in 4 *M* benzene and to ~200 in 12 *M* carbon disulfide. Table IV demonstrates that the secondary hydrogen atoms in 2,4-dimethylpentane and 2,2,4-trimethylpentane are quite normal but that the tertiary hydrogen atoms have an unusually low reactivity, particularly in the solvents that complex chlorine atoms. In 2,4,4-trimethylpentane the tertiary hydrogen atom is somewhat less than 30% as reactive as expected in carbon tetrachloride solution. Toward the chlorine atom complexed in 4 *M* benzene solution, the tertiary hydrogen is about 15% as reactive as expected while toward the chlorine atom in 12 *M* carbon disulfide solution the reactivity is less than 10% of the expected value. This result is explicable in terms of the preferred conformation expected for 2,4-dimethylpentane (1) and 2,2-4-trimethylpentane (2) on the basis of elementary consideration of nonbonded interactions. Although nonbonded interactions would be relieved by attack of chlorine atoms at the secondary or tertiary hydrogen atoms to give a planar radical, it is apparent that the free-radical site is not sufficiently developed in the transition state for this effect to be important. The molecular geometry leaves the methylene group open to attack by the chlorine atom or a complexed chlorine atom. The methine hydrogens cannot be easily attacked, particularly if the chlorine atom must approach along the axis of the carbon–hydrogen bond. The increased importance of this effect when the chlorine atom is complexed with benzene or carbon disulfide may be due to the lowered reactivity of the chlorine atom (requiring closer approach to the carbon–hydrogen bond) or to the increased bulk of the complex.

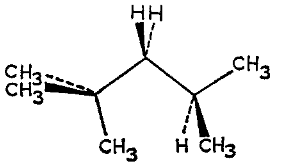
TABLE IV

RELATIVE REACTIVITIES OF HYDROGEN ATOMS

	Solvent		
Hydrocarbon	CCl_4	4 *M* C_6H_6	12 *M* CS_2
	Secondary to Primary		
"Normal"	2–3	5–6	20–25
2,4-Dimethylpentane	2.5 ± 0.1	5.5 ± 0.1	20 ± 1
2,2,4-Trimethylpentane	2.7 ± 0.1	6.0 ± 0.1	20 ± 2
	Tertiary to Primary		
"Normal"	4–5	16–20	200–225
2,4-Dimethylpentane	2.4 ± 0.01	6.5 ± 0.1	30 ± 1
2,2,4-Trimethylpentane	1.2 ± 0.2	2.8 ± 0.1	17 ± 1

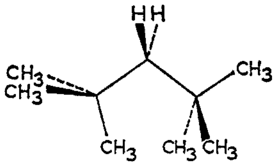


1



2

For 2,2,4,4-tetramethylpentane we might expect a preferred conformation, 3. In 3 the methylene group



3

is not particularly hindered and a normal reactivity is observed. The value of $k_{\text{sec-H}}/k_{\text{cyclohexane-H}}$ is 0.68 in carbon tetrachloride and 0.91 in 4 *M* benzene. In carbon tetrachloride the primary hydrogens are about as reactive as normal primary hydrogen atoms ($k_{\text{prim-H}}/k_{\text{cyclohexane-H}} = 0.34$),[8] but in 4 *M* benzene this value is 0.11 instead of the expected 0.2. This suggests hindrance to methyl attack in 3 due to the crowding of three methyl groups at the back of the molecule.

Insertion of a second methylene group between the tertiary or quaternary centers reduces the crowding at the back of these molecules and normal reactivity of methine hydrogen atoms is observed in 2,5-dimethylhexane and 2,2,5-trimethylhexane.[5]

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[8] In 2,4-dimethylpentane and 2,2,4-trimethylpentane this value is 0.41 and 0.44, respectively.