ports some typical results on the recovery and analysis of synthetic mixtures of the diisobutylenes. Similar results were obtained in recovery experiments for other olefins.

In addition to demonstrating the absence of any isomerization during the isolation procedure, it was established that no isomerization occurred during the hydrolysis. To typical reaction mixtures containing dimethylneopentylcarbinyl chloride and the corresponding bromide were added carefully weighed amounts of 2,4,4-trimethyl-2-pentene. In the case of the chloride the product isolated contained 51.5% of the 1-olefin as compared to a value of 50.5% calculated assuming the usual product with no isomerization of the added olefin. For the bromide, there was observed 53.0%, as compared to a value of 53.4% calculated on the same basis.

No attempt was made to develop as satisfactory a quantitative procedure for the recovery of the butenes and the pentenes from the solvolysis of the tosylates in anhydrous acetic acid. However, it was demonstrated that no isomerization of the olefins occurred under the solvolysis conditions. Of 2.0 ml. of 1-pentene, $n^{20}D$ 1.3714, added to a typical reaction mixture, there was recovered 1.4 ml. of olefin (70%), $n^{20}D$ 1.3714.

TABLE IV

ELIMINATION EXPERIMENTS

Compound	Wt. of halide, g.	Reaction time, hr.[a]	Olefin yield, g.	%	$n^{20}D$
t-Amyl bromide	20.56	12	4.3[b]	30.8	1.3865
Dimethylisopropylcarbonyl bromide	22.45	25	6.75	58.9	1.4083
Diethylmethylcarbinyl bromide	22.45	11	4.64	40.5	1.4026
Dimethylneopentylcarbinyl chloride	10.00	148	4.57	60.5	1.4100
bromide	10.00	48	3.52	60.4	1.4100
iodide	10.00	1	2.63	56.3	1.4101

[a] Estimated for a minimum of 98–99% reaction. [b] Ml.; measured by volume because of the high volatility of the pentenes.

Elimination Experiments for Tertiary Halides.—A typical experiment follows. In a round-bottomed flask were placed 20.6 g. (0.13 mole) of *t*-amyl bromide, 21.3 g. (0.14 mole) of triethanolamine and 400 cc. of 85% *n*-butyl Cellosolve. The reaction mixture was placed in a constant temperature bath at 25° for 60 hours, representing the time estimated from the rate data for 98% reaction. During this time large crystals of the hydrobromide of triethanolamine separated from the solution. The flask was then attached to the Todd micro column and heated. A total of 4.3 cc. of olefin distilled over (below 35°) into the ice-cooled receiver. The olefin was separated from a droplet of water, dried over anhydrous magnesium sulfate, weighed, and its refractive index measured.

Data for one experiment for each of the tertiary halides are presented in Table IV.

The following refractive indices ($n^{20}D$) of the pure olefins were utilized to estimate the compositions of the olefin fractions[13]: 2-methyl-1-butene, 1.3778; 2-methyl-2-butene, 1.3874; 2,3-dimethyl-1-butene, 1.3904; 2,3-dimethyl-2-butene, 1.4122; 2,4,4-trimethyl-1-pentene, 1.4086; 2,4,4-trimethyl-2-pentene, 1.4160.

Elimination Experiments for the Tosylates.—The mixture of 100 ml. of glacial acetic acid, 4.20 g. of potassium acetate and 2 ml. of acetic anhydride was heated under reflux for 3 hours. The solution was cooled to room temperature and 10.0 g. of 2-butyl tosylate was added. The solution was again heated under reflux (118°) for 3 hours and the olefin evolved was collected in a U-tube at −80°. This sample was kindly analyzed for us by Dr. E. D. Tucker and his associates of the Standard Oil Company (Indiana) utilizing infrared absorption.

The similar solvolysis of 46.2 g. (0.2 mole) of 2-pentyl tosylate in 300 ml. of anhydrous acetic acid resulted in the isolation of 3.5 g., 25%, of olefin ($n^{20}D$ 1.3792) which was analyzed by infrared. The data on the olefin composition are reported in Table III.

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[13] "Selected Values of Properties of Hydrocarbons," American Petroleum Institute Research Projects 44 and 45.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. II. The Effect of the Steric Requirements of Alkyl Substituents upon the Extent and Direction of Unimolecular Elimination in the Solvolysis of Tertiary Alkyl Bromides

BY HERBERT C. BROWN AND M. NAKAGAWA[1]

RECEIVED OCTOBER 21, 1954

The solvolysis of the group of *t*-alkyl bromides, $RCH_2CBr(CH_3)_2$ with R = Me, Et, *i*-Pr, *t*-Bu, was studied in order to obtain information on the effect of the steric requirements of the group R on (1) the rate of solvolysis, (2) the yield of olefin in the reaction and (3) the ratio of 1- to 2-olefin in the product. The rate of solvolysis changes in a relatively minor manner from R = Me (k_1 0.387 hr.$^{-1}$) to Et (0.296) to *i*-Pr (0.697), but increases sharply with R = *t*-Bu (k_1 4.71 hr.$^{-1}$). This sharp increase is in accord with the large strain postulated for homomorphs of di-*t*-butylmethane. The yield of olefin also increases with the increasing steric requirements of R: Me, 27%; Et, 32.5%; *i*-Pr, 46%; *t*-Bu, 57%. Finally, the ratio of 1- to 2-olefin changes in the direction to be expected in view of the increasing strain in the 2-olefin resulting from steric interaction between the group R and CH_3:R = Me, 0.27; Et, 0.41; *i*-Pr, 0.70; *t*-Bu, 4.26. The sharp increase with R = *t*-Bu is attributed to the large steric requirements of *t*-Bu and the fact that the strain cannot be reduced by rotation of the alkyl group. It is concluded that the phenomena observed in this family of compounds are in excellent agreement with the postulated effects of steric strains on the solvolytic behavior of tertiary halides.

The solvolysis of the dimethylneopentylcarbinyl halides proceeds to give 81% of 2,4,4-trimethyl-1-pentene and 19% of the 2-isomer.[2–4] This predominant formation of the 1-olefin (Hofmann-type elimination) constitutes an important exception to the proposal by Hughes, Ingold and their co-workers[5] that unimolecular eliminations should invariably proceed to give the most branched olefin (Saytzeff-type elimination). It is important that the factors which are responsible for this exception be thoroughly understood.

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[1] Post-doctorate assistant at Purdue University, 1953–1954, in part on a contract supported by the Office of Naval Research, and in part on a research grant supported by the National Science Foundation.

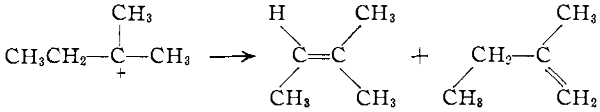
[2] H. C. Brown and H. L. Berneis, THIS JOURNAL, **75**, 10 (1953).

[3] E. D. Hughes, C. K. Ingold and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953).

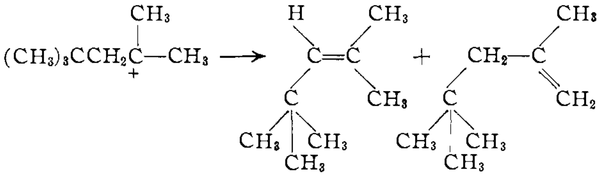
[4] H. C. Brown and I. Moritani, THIS JOURNAL, **77**, 3607 (1955).

[5] E. D. Hughes and C. K. Ingold, *et al.*, *J. Chem. Soc.*, 2093 (1948).

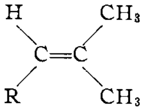
It was proposed that steric strains are responsible for the change in the type of elimination from Saytzeff to Hofmann.[2,4] In elimination from the *t*-amylcarbonium ion, the 2-olefin is formed preferentially. The 2-olefin is thermodynamically more stable than the 1-olefin,[6] presumably as a result of electromeric interactions of the three methyl substituents with the double bond.[5] The steric interactions of the two *cis*-methyl groups in the 2-olefin are presumably too small to overcome the hyperconjugative stabilization.



On the other hand, similar elimination from the diisoöctylcarbonium ion would result in a 2-olefin containing *t*-butyl and methyl groups *cis* to each other. There is evidence that interactions between such groups are quite large. It therefore is proposed that the steric interactions are sufficiently large as to overcome the greater hyperconjugative stabilization of the 2-olefin and render the 1-olefin the stabler of the two. The carbonium ion then undergoes elimination to form the 1-olefin preferentially.



If this interpretation is valid,[7] then the steric interactions should increase in the olefin with the increasing steric requirements of the group R (Me < Et < *i*-Pr << *t*-Bu).



Consequently, if the explanation is valid, there should be observed a regular trend from predominant Saytzeff elimination to predominant Hofmann elimination in the solvolysis of the series of tertiary bromides, $RCH_2CBr(CH_3)_2$, with R = Me, Et, *i*-Pr and *t*-Bu. (It is believed that hyperconjugative stabilization of the incipient double bond in the carbonium ions, $RCH_2C^+(CH_3)_3$, will not be altered significantly by the changes in structure of the alkyl groups R.) Accordingly, a study of the solvolysis of this closely related group of *t*-alkyl bromides was undertaken, utilizing the techniques previously developed.[4]

Results

The rates of solvolysis of the *t*-alkyl bromides were determined in 85% aqueous *n*-butyl Cellosolve. It will be observed that the rate constants do not differ greatly for R = Me, Et and *i*-Pr, but show a sharp increase for R = *t*-Bu (Table I).

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE SOLVOLYSIS OF THE ALKYLDIMETHYLCARBINYL BROMIDES IN 85% *n*-BUTYL CELLOSOLVE AT 25.0°

t-Bromide, $RCH_2CBr(CH_3)_2$	R	k_1, hr.$^{-1}$
t-Amyl	Me	0.387[a]
Dimethyl-*n*-propylcarbinyl	Et	.297
Dimethylisobutylcarbinyl	*i*-Pr	.697
Dimethylneopentylcarbinyl	*t*-Bu	4.71[b]

[a] Ref. 4: 0.385. [b] Ref. 4: 4.70.

Solvolyses were run with 0.1–0.25 mole of *t*-alkyl bromide in the 85% aqueous *n*-butyl Cellosolve. The olefin formed in the solvolysis was distilled out of the reaction mixture, the yield carefully established in representative experiments carried out under identical conditions and the olefin composition established by both refractive index and infrared measurements. The results are summarized in Table II.

TABLE II

YIELD AND COMPOSITION OF OLEFINS FORMED IN THE SOLVOLYSIS OF ALKYLDIMETHYLCARBINYL BROMIDES IN 85% *n*-BUTYL CELLOSOLVE AT 25°

			Composition		
t-Bromide, $RCH_2CBr(CH_3)_2$	R	Yield, %	1-Olefin	2-Olefin	Ratio
t-Amyl	Me	27[a]	21[a]	79	0.27
Dimethyl-*n*-propylcarbinyl	Et	32.5	29	71	0.41
Dimethylisobutylcarbinyl	*i*-Pr	46	41	59	0.70
Dimethylneopentylcarbinyl	*t*-Bu	57[b]	81[b]	19	4.26

[a] Ref. 4: 30.8% yield; 20% 1-olefin. [b] Ref. 4: 60.4% yield; 82% 1-olefin.

It should be observed that the yield of olefin increases regularly with the steric requirements of the group R. Moreover, the ratio of 1- to 2-olefin in the product increases gradually from R = Me to R = *i*-Pr, with a very sharp increase with R = *t*-Bu.

Discussion

The rates of hydrolysis reveal relatively small changes in the series R = Me, Et, *i*-Pr. This supports the postulate that increased branching of R should not have any important effect on the degree of hyperconjugative stabilization of the carbonium ions $RCH_2C^+(CH_3)_2$. (It also lends support to the belief that increased branching in R should have little effect in altering the degree of hyperconjugative stabilization of the incipient double bond in the transition state leading to elimination.) Only when R becomes *t*-Bu is there observed a sharp increase in the hydrolysis rate. It does not appear reasonable to attribute this increase in rate to a sudden increase in hyperconjugative stabilization of the carbonium ion provided by the *t*-butyl group.

Dimethylneopentylcarbinyl bromide is a homomorph of di-*t*-butylmethane, a molecule for which strains of 5.0–5.5 kcal./mole have been estimated.[8] The large increases in the rates of hydrolysis in halides of this structure have been attributed to the relief of B-strain accompanying the ionization of the halide.

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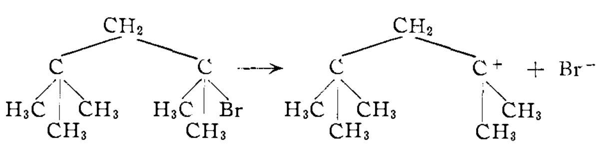
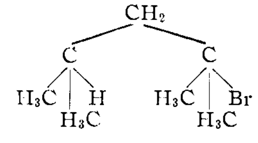
[6] J. Conant and G. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

[7] An alternative explanation has been suggested (ref. 3). Discussion will be deferred until the summary paper of this group: H. C. Brown and I. Moritani, THIS JOURNAL, **77**, 3623 (1954).

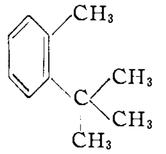
[8] H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

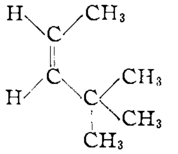


With R = *i*-Pr, the strain can be relieved by a simple rotation of the alkyl group and the strain will be greatly diminished. Consequently, the driving force provided by the relief of steric strain in this case will be far smaller.

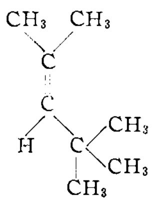


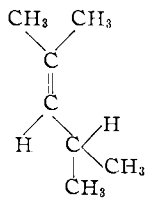
The same arguments can be applied to the interpretation of the relatively small increases in the 1- to 2-olefin ratio observed in the case of R = Me, Et, *i*-Pr as compared to the large increase for R = *t*-Bu (Table II). There now exists considerable evidence that the strain in homomorphs of *o*-*t*-butyltoluene is in the neighborhood of 6.0 kcal./mole.[8,9] It may be expected that the strain in *cis*-*t*-butylmethylethylene also will be of this order of magnitude.



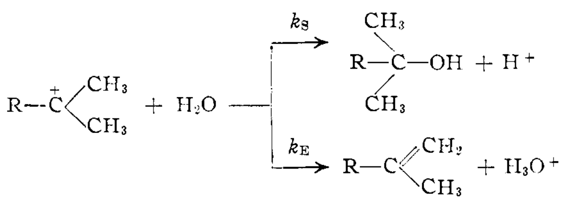


However, replacement of the *t*-butyl group by an isopropyl group permits a marked reduction in the strain by a simple rotation of the alkyl group. In the case of the *t*-butyl group mere rotation does not alter the effective strain. Consequently, the vast difference in the effect of R = *t*-Bu as compared to R = *i*-Pr on the ratio of the 1- to 2-olefin is quite reasonable in terms of the steric interpretation we have advanced.[10]





Finally, the relatively gradual increase in the yield of olefin in the series also appears to be explicable in terms of the operation of steric forces. The yield of olefin will depend upon the relative rate of substitution of the carbonium ion, compared with the relative rate of elimination.



The greater the steric requirements of R, the slower should be the value of k_S and the larger would be expected to be the value of k_E. Unfortunately, nothing is presently known about the effect of structure on the magnitude of k_E. However, evidence has been presented that an increase in the steric requirements of the alkyl groups attached to a tertiary carbonium ion leads to a marked decrease in the substitution rate.[11] A decrease in k_S with the increasing steric requirements of R would lead to the observed change, a decrease in the substitution product and an increase in the olefin produced. (This assumes that k_E will not decrease sharply with increasing steric requirements of R. No theoretical basis for a decrease of this kind is apparent.)

The carbonium ion is much less crowded than the original tetrahedral molecule. Consequently, an increase in the steric requirements of R would be expected to be much less important in the ion than it is in the original halide. For this reason the effect of the steric requirements of R on the yield of olefin should be considerably less than their effect both upon the solvolysis rate and the ratio of 1- to 2-olefin in the product.

It is concluded that the data are clearly consistent with the postulated effects of steric strains on rates of solvolysis and the extent and direction of olefin formation.[12,13]

Experimental Part

Materials.—The *t*-amyl alcohol was the commercial product, fractionated through an efficient column. Dimethyl-*n*-propylcarbinol and dimethylisobutylcarbinol were prepared by the reaction of *n*-propylmagnesium bromide and isobutylmagnesium bromide on acetone. The yields were 65 and 27%, respectively. The dimethylneopentylcarbinol was prepared by adding hydrogen chloride to purified diisobutylene, followed by neutral hydrolysis of the chloride.[2] The alcohols were converted into the tertiary bromides in yields of approximately 90% by treating with hydrogen bromide to saturation, followed by distillation in all glass equipment under reduced pressure. The physical constants observed for the alcohols and bromides are listed in Table III. Pure samples of the individual olefins for infrared analysis of the olefin products were obtained from the Bureau of Standards and A.P.I. Project No. 45 at Ohio State University. This valuable assistance is gratefully acknowledged.

Rates of Solvolysis.—The rate data were determined as previously described.[4,12] The 85% *n*-butyl Cellosolve was prepared as previously reported.[4] The solvent exhibited the constants $d^{25}{}_4$ 0.9219, $n^{20}{}_D$ 1.4095.

Elimination Experiments.—In attempting to apply the procedure previously developed,[4] a difficulty was encountered. The *n*-butyl Cellosolve available apparently contained a minor amount of an impurity which liberated acetaldehyde slowly as the solvent was heated to distil out the olefin. The following procedure, representative of that used for all the compounds, overcame the difficulty at some cost in the ease of operation and in the quantitativeness of the olefin recovery.[14]

In a 500-ml. round-bottomed flask was placed 0.1 mole of the *t*-alkyl bromide, 0.11 mole of triethanolamine (b.p. 196–197° (6 mm.)) and 250 ml. of the 85% *n*-butyl Cello-

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[9] Unpublished work with D. Gintis and L. Domash.

[10] For simplicity, this discussion has been based upon the consideration of the relative strain in the two isomeric olefinic products. In actual fact the relative yields of the two olefins will be determined by the relative stabilities of the two different transition states for the elimination. It is reasonable to expect that the relative stabilities of the two products will be reflected in a corresponding difference in the relative stabilities of the two related transition states.

[11] H. C. Brown and R. B. Kornblum, THIS JOURNAL, **76**, 4510 (1954).

[12] H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

[13] H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950).

[14] Recovery of olefin by this procedure ran approximately 4% lower than those previously realized (Table II).

TABLE III

PHYSICAL PROPERTIES OF MATERIALS

Compound	Observed constants B.p. °C.	Mm.	$n^{20}D$	Literature constants B.p. °C.	Mm.	$n^{20}D$	Ref.
t-Amyl alcohol	101	746	1.4043	102	746	1.4020	[a]
Dimethyl-*n*-propylcarbinol	49.5	27.5	1.4105	117–122	760	(1.4107)[b]	[b]
Dimethylisobutylcarbinol	54	28	1.4162	133.1	760	1.4165	[c]
Dimethylneopentylcarbinol	60.5	28.4	1.4280	146–146.5	750	(1.4256)[d]	[d]
t-Amyl bromide	51.5	110	1.4410	103.5–104	744	1.4421	[e]
Dimethyl-*n*-propylcarbinyl bromide	47	38	1.4442	77–78	145	(1.442)[g]	[f,g]
Dimethylisobutylcarbinyl bromide	46	20	1.4461	83–84	100	1.4465	[c]
Dimethylneopentylcarbinyl bromide	61.5	15	1.4567	62–63	18	1.4557	[e]

[a] R. C. Huston and R. G. Brandt, *J. Org. Chem.*, **15**, 1211 (1950). [b] F. Krollpfeiffer and H. Seebaum, *J. prakt. Chem.*, **119**, 131 (1928). Refractive index value is n^{20}He. [c] H. de Graef, *Bull. soc. chim. Belg.*, **40**, 315 (1931). [d] Ref. 2. Refractive index value is n^{25}D. [e] H. C. Brown and A. Stern, THIS JOURNAL, **72**, 5068 (1950). [f] A. Faworski, *J. Russ. Phys. Chem. Soc.*, **50**, 43 (1918). [g] A. Deschamp, THIS JOURNAL, **42**, 2671 (1920). Refractive index value is n^{23}D.

TABLE IV

SUMMARY OF EXPERIMENTAL CONDITIONS AND YIELD AND COMPOSITION DATA ON THE OLEFINS FORMED IN THE SOLVOLYSIS OF ALKYLDIMETHYLCARBINYL BROMIDES IN *n*-BUTYL CELLOSOLVE AT 25°

t-Bromides	$RCH_2CBr(CH_3)_2$ g.	mole	Reaction time, hr.	Solvent, ml.	Triethanolamine g.	moles	Olefin, g.	Yield, %	Olefin $n^{20}D$	Compn. % 1-	2-
t-Amyl	30.2	0.20	60	500	32.8	0.22	3.53	26	1.3853	21	79
	37.7	.25	60	625	41.0	.27	4.94	28	1.3853	21	79
	15.1	.10	60	250	16.4	.11			1.3855	20	80
	15.1	.10	60	250	16.4	.11			1.3854	20	80
									IR	19	81
Dimethyl-*n*-propylcarbinyl	33.0	.20	60	500	32.8	.22	5.22	31	1.3976	31	69
	33.0	.20	60	500	32.8	.22	5.63	34	1.3978	29	71
	16.5	.10	51	250	16.4	.11			1.3979	28	72
	11.4	.07	216	200	16.4	.11			1.3978	29	71
									IR	28	72
Dimethylisobutylcarbinyl	17.9	.10	48	250	16.4	.11	4.50	46	1.4016	42	58
	17.9	.10	40	250	16.4	.11			1.4017	41	59
									IR	40	60
Dimethylneopentylcarbinyl	19.3	.10	24	250	16.4	.11	6.34	57	1.4096	86	14
	20.9	.117	24	293	19.2	.13	7.47	57	1.4100	81	19
	19.3	.10	20	250	16.4	.11			1.4099	82	18
									IR	85	15

solve. The mixture was maintained at 25° for 24 to 60 hr. The triethanolamine hydrobromide was collected on a sintered glass filter with the aid of slight excess air pressure and washed with small amounts of the solvent. The combined solution was mixed with 50 ml. of water and distilled through a short Vigreux-type distillation head, until the distillate was homogeneous. The distillate was collected in a strongly cooled receiver to minimize losses. The organic layer of the distillate was separated from the aqueous layer and dried over anhydrous potassium carbonate. The dried distillate was separated from the drying agent by decantation and carefully redistilled through the Todd microcolumn, using an appropriate water-soluble "chaser" (ethanol or pyridine). The distillate was washed with several portions of cold water to remove traces of aldehyde and the "chaser," dried over anhydrous magnesium sulfate and weighed. Minor corrections for the amount of olefin absorbed on the drying agents were applied in determining the yield of olefin. Analysis was by refractive index with several checks by infrared analysis.

Numerous control experiments were run to test the adequacy of the isolation and analytical procedures. Typical results of similar control experiments are reported in the preceding paper (Table I).[4]

The following $n^{20}D$ values for the olefins[15] were used in the analyses: 2-methyl-1-butene, 1.3778; 2-methyl-2-butene, 1.3874; 2-methyl-1-pentene, 1.3914; 2-methyl-2-pentene, 1.4004; 2,4-dimethyl-1-pentene, 1.3986; 2,4-dimethyl-2-pentene, 1.4038; 2,4,4-trimethyl-1-pentene, 1.4086; 2,4,4-trimethyl-2-pentene, 1.4160.

The experimental results are summarized in Table IV.

The values for the extent and direction of olefin formation in Tables I and II represent the best values in our opinion based upon both the data in Table IV and those elsewhere reported.[4]

LAFAYETTE, INDIANA

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[15] "Selected Values of Properties of Hydrocarbons," American Petroleum Institute Research Projects 44 and 45.