TABLE I

ACTIVITY DISTRIBUTIONS IN THE 1-CHLOROPROPANE FROM REACTION OF CYCLOPROPANE WITH HCl-*t*

	c-C_3H_6 + $ZnCl_2$ − HCl-*t*[a]				*c*-C_3H_6 + HCl-*t*				*c*-C_3H_6 + $AlCl_3$ − HCl-*t*			
		t-Distribution, %				*t*-Distribution, %				*t*-Distribution, %		
Run	Yield,[b] g	C-1	C-2	C-3	Yield,[b] g	C-1	C-2	C-3	Yield,[b] g	C-1	C-2	C-3
1	4.6	38.6	16.6	44.7	3.4[c]	37.7	18.2	44.1	3.5[c]	33.3	21.4	45.3
2	4.8	37.2	19.7	43.1	5.7	37.7	15.6	46.7	5.9	33.8	22.8	43.4
3	5.8	37.7	18.8	43.5	4.8	38.3	17.1	44.6				

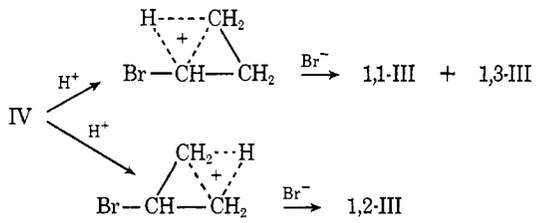
[a] From ref 1. [b] Estimated by isotope dilution calculations. [c] The *c*-C_3H_6 was bubbled through the reaction mixture for 16 hr; in the other experiments, the bubbling time was 24 hr.

TABLE II

DATA FROM REACTIONS BETWEEN BROMOCYCLOPROPANE (IV) AND HBr WITH OR WITHOUT THE PRESENCE OF $AlCl_3$

	Reaction time, hr	Recovered IV, %	Dibromopropane obtained, % 1,1-	1,2-	1,3-
No $AlCl_3$	1	95.8	0.8	1.1	...
	2	86.7	2.9	3.7	Trace
	6	71.6	9.0	10.4	3.5
	24	53.4	21.5	14.5	6.5
$AlCl_3$	2	69.6	6.6	8.1	Trace
	12	64.3	12.9	15.3	0.5

SCHEME II



from the addition of DCl to methylcyclopropane as the result of the addition of D^+ to methylcyclopropane to give the 2-butyl cation directly or *via* a short-lived nonisomerizing protonated methylcyclopropane.

Experimental Section

1-*t*-1-Chloropropane (II-1-*t*).—A mixture of 10.7 g (50 mmol) of 1-*t*-1-propyl tosylate and 11.0 g (100 mmol) of $CaCl_2$ in 75 ml of ethylene glycol was placed in a flask fitted for distillation. The flask was heated at 70–75° for 3 hr while a slow stream of nitrogen was passed over the reaction mixture to sweep out the product. The 1-*t*-1-chloropropane so obtained (in about 75% yield) was passed through anhydrous $CaCl_2$ and collected in a receiver cooled in Dry Ice–acetone.

Treatment of 1-*t*-1-Chloropropane (II-1-*t*) with $ZnCl_2$–HCl.—A mixture of 8.0 g (102 mmol) of II-1-*t*, 20.4 g (150 mmol) of $ZnCl_2$, and 12.5 ml (150 mmol) of 12 *M* HCl in a 50-ml flask was heated under reflux at 50 ± 2° for 100 hr. An efficient condenser was employed and the top of the condenser was loosely stoppered to minimize the loss of chloride. After the period of gentle refluxing was completed, about 2.0 g of II-1-*t* was recovered. Analysis by vpc showed the absence of 2-chloropropane. In a number of experiments starting with II-1-*t* of specific activities varying from about 200,000 to 1,200,000 cpm per mmol, the recovered II-1-*t* was converted to 1-*t*-1-propanol, which on oxidation gave inactive propanoic acid,[1] showing no rearrangement of the *t*-label to C-2 and C-3. The same results were obtained when the mixture of II-1-*t* and $ZnCl_2$–HCl in a sealed tube was placed in a hydrogenation bomb and then shaken and heated at 50 ±2° for 100 hr.

Reaction between Cyclopropane (I) and HCl.—I was bubbled through 25 ml of 12 *M* HCl-*t* at room temperature for 24 hr, and the product obtained was worked up and degraded as described previously.[1] Vpc analysis of the 1-chloropropane so obtained showed the absence of any 2-chloropropane. When the reaction was carried out in the presence of $AlCl_3$, 5.0 g of anhydrous $AlCl_3$ per 100 g of 12 *M* HCl was employed. Since the solubility of $AlCl_3$ in 12 *M* HCl was low, the suspension was stirred by a magnetic stirrer during the passage of I through the mixture. Vpc analysis of the product by an 8 ft × 0.25 in. stainless steel column packed with 25% FFAP on 60–80 mesh Chromosorb W showed that the 1-chloropropane contained about 3–4% 2-chloropropane.

Reaction between Bromocyclopropane (IV) and HBr.—The HBr solution was prepared by bubbling gaseous HBr into distilled water cooled at about 0° until a saturated solution was obtained. Titration showed the HBr concentration as 68%. The same batch of HBr solution was used in all the experiments.

A mixture of 2.42 g (20 mmol) of IV and 10 ml of 68% HBr, without or with the presence of 1.5 mmol of $AlCl_3$, was placed in a 50-ml flask fitted with a reflux condenser and was stirred at room tmperature for the desired length of time. Water was then added and the resulting material was extracted with ether. The extract was washed with water uutil free of acid, dried over anhydrous $MgSO_4$, and analyzed by vpc for IV, 1,1-III, 1,2-III, and 1,3-III by the FFAP column described above. All identifications and calibrations were based on chromatographically pure samples of IV, 1,1-III, 1,2-III, and 1,3-III. 1,1-III was prepared by the method of Stevens and coworkers,[9] while the other authentic samples were purchased commercially.

Registry No.—I, 75-19-4; hydrochloric acid, 7647-01-0; IV, 4333-56-6; hydrobromic acid, 10035-10-6.

Acknowledgment.—The financial support given by the National Research Council of Canada is gratefully acknowledged.

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Alkylation of Naphthalene with Alkenes

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Whitmore and James[2] reported the formation of 2-*t*-butylnaphthalene plus uncharacterized higher alkylation products in the aluminum chloride catalyzed reaction of naphthalene with isobutylene. Other reports of the alkylation of naphthalene with olefins, alcohols, or alkyl halides also indicate preferential formation of the 2 isomer.[3,4] This preference for the 2 isomer has been argued on steric grounds in the case of bulky olefin–catalyst complexes and on the basis of rearrangement of the kinetically favored 1 isomer.

This communication reports work undertaken to investigate the alkylation of naphthalene with olefins under nonisomerizing conditions and thereby to deter-

(1) To whom correspondence should be addressed at Wright Laboratory, Rutgers, The State University, New Brunswick, N. J. 08903.

(2) F. C. Whitmore and W. H. James, *J. Amer. Chem. Soc.*, **65**, 2088 (1943).

(3) "Friedel–Crafts and Related Reactions," Vol. II, G. Olah, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter XIV.

(4) H. E. Nursten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).

mine the kinetically controlled isomer distribution. For this purpose, BF_3–H_3PO_4 was chosen as the catalyst system, work by Topchiev and his coworkers[5,6] having shown alkylation to occur in high yields with lack of side reactions. The alkylation of benzene with propylene and the absence of transalkylation have been reported using this catalyst system.[3] The data obtained for six olefins are shown in Table I.

TABLE I
MONOALKYLATION OF NAPHTHALENE[a]

Alkene	Mono,[b] %	R	1, %	2, %
Propylene	69	—CHMe$_2$	70	30
1-Butene	76	—CHEt (Me)	74	26
cis-2-Butene	81	—CHEt (Me)	72	28
trans-2-Butene	83	—CHEt	70	30
Isobutylene	76	—CMe$_3$	0	100
Diisobutylene	81	—CMe$_3$	0	100

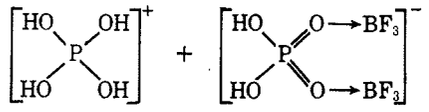
[a] Temperature 5–10°, catalyst BF_3–H_3PO_4, reaction time 6 hr. [b] Mole per cent of monoalkylate in a mixture of mono- and dialkylate. The mixture accounts for 75–90% of the weight of crude alkylate.

The mono-, di-, and polyalkylation products were separated by fractional distillation and the 1 and 2 isomer by vapor phase chromatography. The products were characterized by a combination of infrared and nuclear magnetic resonance spectroscopy.

It was shown that, under the conditions of the reaction, none of the 1 isomers rearranged. The 1-*t*-butylnaphthalene required for this purpose was prepared by the method of Illingworth and Peters.[7]

Topchiev and coauthors[5] review coordination compounds of the type formed between equimolar amounts of boron trifluoride and phosphoric acid. Greenwood and Thompson[8] postulate an equilibrium between the complex **1** of boron trifluoride and phosphoric acid and its ionic form **2**.

1



2

The electrophile in this Friedel–Crafts alkylation might be expected to be of form **3** resembling the 1:1:1

$$RCH{=}CH_2 + H_3PO_4 + BF_3 \rightleftharpoons RC^+HCH_3(H_2PO_4BF_3)^-$$

3

complex reported by Olah and coworkers[9] for α olefins, boron trifluoride, and hydrogen fluoride.

An attractive mechanism for the Friedel–Crafts alkylation of aromatics by olefins postulates an attack by the aromatic ring on the olefin–catalyst complex.[10] If such a mechanism were operative in the alkylation of naphthalene with olefin–catalyst complexes, one would anticipate substantial dependence upon steric factors and the degree of ionic character in the olefin–catalyst complex.

The similarity of product distribution for the three butenes suggests the intermediacy of the common ionic species, the *sec*-butyl cation. Also, the equivalence for propylene is not surprising in view of the correspondence in steric requirements between isopropyl and *sec*-butyl groups, reported by Brown.[11] The preferential alkylation at the 1 position is explicable on the basis of the low temperature of the reaction and the lower transition-state energy for the formation of the corresponding naphthalenonium ion complex in a kinetically controlled mechanism. Dewar, Mole, and Warford[12] found partial rate factors of 470 and 50, respectively, for the 1 and 2 positions in the nitration of naphthalene.

The formation of no detectable 1-*t*-butylnaphthalene in the reactions of the isobutylenes suggests that in these cases, for steric reasons, the 2 isomer becomes the exclusive kinetic product. For olefins of size intermediate between isobutylene and 1-butene, it should be possible to approach kinetic equivalence between the 1 and 2 positions in naphthalene. Work in this direction is in progress.

In the reactions of isobutylene and diisobutylene, in addition to predominant 2-*t*-butylnaphthalene, the same variety of minor products was obtained, as shown in Table II.

TABLE II
"BUTYLATION" OF NAPHTHALENE[a]

Naphthalene derivative	With isobutylene, %	With diisobutylene, %
2-*t*-Butyl	70.0	73.4
2-(1,1-Dimethylpropyl)	2.0	4.4
2-(1,1-Dimethylbutyl)	0.6	0.7
2-(1,1,2-Trimethylpropyl)	1.1	0.9
2-(1,1,3-Trimethylbutyl)	1.2	1.0
2,6-Di-*t*-butyl	15.6	11.6
2,7-Di-*t*-butyl	8.8	8.0

[a] Temperature 5–10°, catalyst BF_3–H_3PO_4, reaction time 6 hr.

The structures of these products were determined spectroscopically, and it is believed that they arise through a polymerization–depolymerization mechanism similar to that reported by Hofmann and Schriesheim.[13]

In summary, it has been shown that even with relatively large olefin–catalyst complexes the 1 isomer is the kinetically favored product in the Friedel–Crafts alkylation of naphthalene.

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(6) A. V. Topchiev, S. V. Zavgorodnii, and V. G. Kryuchkova, "Alkylation with Olefins," Elsevier Publishing Co., 1964, Chapter II.
(7) E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).
(8) N. N. Greenwood and A. Thompson, *ibid.*, 3493 (1959).
(9) G. A. Olah, H. W. Quinn, and S. J. Kuhn, *J. Amer. Chem. Soc.*, **82**, 426 (1960).
(10) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).
(11) H. C. Brown, *J. Chem. Ed.*, **36**, 424 (1959).
(12) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).
(13) J. E. Hofmann and A. Schriesheim, *J. Amer. Chem. Soc.*, **84**, 953, 957 (1962).

Experimental Section

General.—Diisobutylene (Atlantic Richfield Co.), boron trifluoride (Allied Chemical Co.), and naphthalene (Fisher Scientific Co.) were used without purification. All other chemicals were of the highest purity available from the Matheson Chemical Co.

Boiling points are uncorrected. Infrared spectra were measured as neat films or in carbon tetrachloride solutions on a Beckman IR-10 instrument.

The vpc analyses were done on a Varian-Aerograph Model 1520 instrument under the following conditions.

Nuclear magnetic resonance spectra were obtained on Varian A-60 and HA-100 instruments. Microanalyses were performed by Micro-Analyses, Inc., Wilmington, Del.

Boron Trifluoride–Phosphoric Acid Complex.—In a dry 1000-ml three-neck flask, equipped with a thermometer, a gas dispersion tube, and a calcium chloride tube, 300 g (2.60 mol) of 85% phosphoric acid was saturated with boron trifluoride. The product, 585 g, sp gr 1.84 (30°), corresponded to an equimolar mixture.

Alkylation of Naphthalene. Standard Procedure.—Over a period of 60 min, 0.60 mol of the olefin was added at a constant rate to a slurry of 51 g of the catalyst and 64 g (0.50 mol) of naphthalene in a 500-ml three-neck flask equipped with a thermometer, reflux condenser, stirrer, gas inlet tube, and cooling bath. The reaction temperature was held at 5–10°. This procedure was repeated three more times by sequential additions of these quantities of the reactants.[14] Finally, the reaction mixture was held at 5–10° for 2 additional hr. The organic layer was separated from the lower catalyst layer, washed with water, 5% sodium hydroxide, and again with water, and dried over anhydrous sodium sulfate to yield a crude mixture, A, of naphthalene and mono- and dialkylnaphthalenes. Vpc (column A, 1 μl) gave the distribution of these three components. For isolation of the monoalkylnaphthalenes, it was found expedient to remove the naphthalene and dialkylnaphthalenes prior to preparative vpc analysis by vacuum distillation (1–10 mm) of A using a 12-in. Vigreux column followed by a redistillation through a Nester and Faust 24-in. Teflon spinning-band column to give purified mixture B. The 1- and 2-monoalkylnaphthalenes were separated by vpc through larger columns (Table III).

TABLE III

Column	Length, ft	Diameter, in.	Type	Helium rate, ml/min	Temp, °C: Injection	Temp, °C: Column
A	20	1/4	Apiezon L (20%)	100	290	230–300
B	20	3/8	EG-SP-Z (20%)	150	290	188
C	30	1/4	SE-52 (10%)	150	300	254
D	50	3/8	Apiezon L (20%)	170	290	232

Table IV gives a summary of the results of using this procedure with the six alkenes.

TABLE IV

COMPOSITION OF CRUDE ALKYLATE

Alkene	Wt of A, g	Vpc analysis,[a] mol %: Naphthalene	Dialkyl	Monoalkyl
Propylene	357	23.5	25.6	62.9
1-Butene	347	6.7	17.7	75.6
cis-2-Butene	338	9.7	14.0	76.3
trans-2-Butene	336	12.1	12.1	75.6
Isobutylene	388	34.5	12.9	52.6
Diisobutylene	368	39.4	9.4	51.2

[a] Column A (Table III), with results expressed as mole per cent.

In each case, the purified mixture B was separated by preparative vpc to give the data in Table V.

The new compounds reported in these series are as follows.

1-*sec*-Butylnaphthalene.—The ir region of 700–900 cm^{-1} was of particular value[15] in this identification, and the nmr spectra showed the patterns to be expected for *sec*-butyl groups: τ 9.15 (t, CH_3), 8.72 (d, CH_3), 8.0–8.5 (m, CH_2), 6.3–6.8 (m, CH), and 1.8–2.8 (naphthyl CH).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.11; H, 8.74.

(14) This procedure allowed satisfactory mixing of the reactants throughout the entire reaction cycle.

(15) American Petroleum Institute, Infrared Spectral Data, 763, 1980.

TABLE V

MONOALKYLATION PRODUCTS

Alkyl group	Column	Amount injected, μl	Retention time: 1-Alkyl	Retention time: 2-Alkyl
Isopropyl	C	15	81.1	73.2
sec-Butyl	D	40	65.1	68.6
t-Butyl	B	50	47.4[a]	41.3

[a] No 1-*t*-butylnaphthalene is formed in this alkylation. Retention time is for a sample prepared independently by the method of Illingworth and Peters.[7]

2-*sec*-Butylnaphthalene.—The 700–900-cm^{-1} region in the ir showed the expected substitution.[15] The nmr had τ 9.17 (t, CH_3), 8.71 (d, CH_3), 8.0–8.6 (m, CH_2), 7.0–7.6 (m, CH), and 2.1–2.8 (naphthyl CH).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.00; H, 8.91.

Four additional 2-alkylated naphthalenes were obtained in the reactions with both isobutylene and diisobutylene. Due to small quantities obtained (20–40 mg), identification was possible only by nmr, ir, and mass spectra, and is as indicated in Table VI.

TABLE VI

ADDITIONAL 2-ALKYLATED PRODUCTS FROM ISOBUTYLENES

Alkyl compd	Retention time[a]	Molecular formula[b]
1,1-Dimethylpropyl	21.0	$C_{15}H_{18}$
1,1-Dimethylbutyl	24.2	$C_{16}H_{20}$
1,1,2-Trimethylpropyl	26.3	$C_{16}H_{20}$
1,1,3-Trimethylbutyl	27.6	$C_{17}H_{22}$

[a] Column (SE-52), 30 ft × 0.25 in., 35-μl injection. [b] As determined from mass spectrum.

Attempted Isomerization of 1-Alkylnaphthalenes.—The heating of 100-mg samples of 1-*sec*-butyl-, *t*-butyl-, and isopropylnaphthalenes with the catalyst under reaction conditions gave no isomerization which could be detected by vpc.

Registry No.—Naphthalene, 91-20-3; 1-*sec*-butylnaphthalene, 1680-58-6; 2-*sec*-butylnaphthalene, 4614-03-3; 2-(1,1-dimethylpropyl)naphthalene, 20798-05-4; 2-(1,1-dimethylbutyl)naphthalene, 20798-06-5; 2-(1,1,2-trimethylpropyl)naphthalene, 20798-07-6; 2-(1,1,3-trimethylbutyl)naphthalene, 20798-08-7; propylene, 115-07-1; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7.

Acknowledgment.—The invaluable assistance of John Jungnickel of Shell Development Company, for the recording and interpretation of a portion of the nmr and mass spectra, is greatly appreciated.

2,3-Dihydro-1H-imidazo[1,5-*b*]pyrazole-4,6(3aH,5H)-dione

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Our interest in nitrofurantoin[1] and its 3-substituted derivatives[2] has led us to prepare certain of its 5-substi-

(1) The generic name for 1-(5-nitrofurfurylidenamino)hydantoin, The Norwich Pharmacal Co.'s registered trademark of which is Furadantin®; K. J. Hayes, U. S. Patent 2,610,181 (1952).

(2) (a) J. G. Michels, U. S. Patents 3,075,972, 3,075,973, 3,075,974, and 3,097,202 (1963); (b) C. F. Spencer and J. G. Michels, *J. Org. Chem.*, **29**, 3416 (1964).