water. After drying and evaporation of organic phase 0.75 g (74%) of a 3:2 mixture of trans and cis alcohol **27** and **28**, respectively, was obtained. These two alcohols were separated by column chromatography (silica gel, chloroform–2% methanol as eluent): R_f (cis, **28**) 0.35; R_f (trans, **27**) 0.29. NMR ($CDCl_3$) for **27**: δ 4.18 (dd, 1, methine H-3, J = 10 and 5 Hz), 6.11 (dd, 1, olefin H-1, J = 10.5 and 4.5 Hz). NMR ($CDCl_3$) for **28**: δ 4.71 (dd, 1, methine H-3, J = 10 and 5 Hz), 6.21 (t, 1, olefin H-1, J = 8.5 Hz).

Acknowledgment. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No.—**27**, 61045-46-3; **28**, 60996-51-2; silver nitrate; 7761-88-8; *cis*-2-bromocyclonon-1-en-3-ol, 32726-58-2; *cis*-bromocyclodec-1-en-3-ol, 57090-98-9; *trans*-2-bromocyclodec-1-en-3-ol, 57090-97-8; *tert*-butyl alcohol, 75-65-0.

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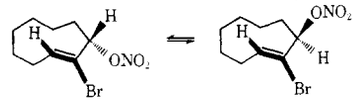

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The NMR spectrum (CCl_4) displayed an olefinic multiplet at δ 6.23, whereas the methine part was splitted in two signals, viz., a triplet at δ 5.33 (J = 5 Hz) and a double doublet at δ 5.02 (J = 10 and 4 Hz).
(7) Excess of silver perchlorate is necessary to obtain a high reaction rate and a quantitative conversion.
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(15) Address correspondence to Organon International B. v., Research and Development Laboratories, RL 312, Dss. The Netherlands.

Specific Ortho Bromination.[1] 2. Aluminum Trichloride Catalyzed Transalkylation

Y. Halpern* and D. Meidar

Casali Institute of Applied Chemistry, the Hebrew University of Jerusalem, Jerusalem, Israel

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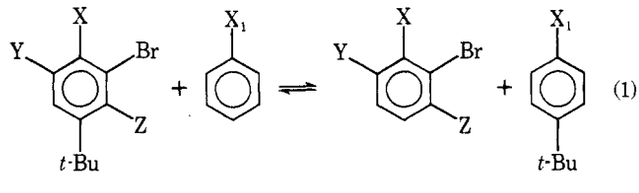
Transalkylation between 2-bromo-4-*tert*-butyl derivatives of substituted benzenes (donors) and various aromatics (acceptors) was found (under the conditions of this study) to be catalyzed by solid $AlCl_3$. The equilibrium constant of the reversible process was determined at different temperatures. The enthalpy of the reaction was calculated and discussed.

Direct bromination of monosubstituted aromatic compounds yields a mixture of the three possible monobrominated isomers. The separation of the isomers in most cases is difficult owing to their similarity in physical properties. In order to overcome this difficulty methods for an indirect bromination specifically at the ortho position have been developed.[1]

Tertiary butyl and other bulky hydrocarbons were used as blocking groups in the synthesis of ortho-disubstituted benzene derivatives. Various catalysts, temperatures, substrates, and solvents were used for the removal of the blocking groups.[2–8]

It has been reported[9–15] that bromine attached to benzene or substituted benzene shifts along the aromatic nuclei or even cleaves under alkylation reaction conditions.

We have recently reported that catalytic amounts of $AlCl_3$ promote the transfer of *tert*-butyl group from the donor to the acceptor, in a reversible process according to eq 1.[1]



(1)

Results and Discussion

At least 5 mol % of $AlCl_3$ is needed to disproportionate bromobenzene to benzene and dibromobenzene.[13] Our results show that transfer of *tert*-butyl group from the donor to the acceptor is accomplished with 1–2 mol % of $AlCl_3$ without concurrent bromine transfer.

Crump,[16] who investigated the $AlCl_3$-catalyzed isomerization of bromotoluenes, suggested that the $AlCl_3$ catalysis is heterogeneous in nature.

Table I. Yields of o-Bromotoluene, after Various Reaction Times, as a Function of Incubation Period[a]

Expt no	16	17	18	19	20	21
Incubation time, h	0	24	48	72	96	144
Reaction time, min	% yield					
5	38.3	38.0	27.0	1.4	0.1	0.1
10	82.8	82.0	47.0	5.5	0.1	0.1
15	88.0	87.0	62.0	10.0	0.1	0.1
20	88.3	88.1	73.0	17.0	0.1	0.1
30	88.6	88.4	85.7	32.2	0.1	0.1
45	88.7	88.5	88.7	60.0	0.1	0.1
60		89.0		79.5	0.1	0.1
90			88.7	86.2	0.3	0.1
150				87.5	0.5	0.1
240					1.0	0.7

[a] 2-Bromo-4-*tert*-butyltoluene, 3.8 ml (20 mmol); benzene, 7.1 ml (80 mmol); $AlCl_3$, 26.7 mg (0.2 mmol); T = 20 °C. Catalyst's particle size 50 μ.

Table II. Yields of o-Bromotoluene, after Various Reaction Times, as a Function of Incubation Period, Catalyst Particle Size 300 μ[a]

Expt no.	23	24	25	26	27	28
Incubation time, h	0	22	48	72	96	144
Reaction time, min	% yield					
5	1.4	17.1	15.5	7.0	3.3	0.1
10	8.8	37.0	31.5	11.9	8.0	0.1
15	19.5	52.5	46.8	19.0	13.7	0.1
20	39.3	66.3	61.6	31.3	19.3	0.1
30	78.3	81.6	80.5	56.5	32.8	0.1
45	87.7	87.4		79.2		0.1
60	88.0		88.7	87.2		0.1
90					81.3	0.1
120	88.6					0.1
150					87.2	0.3
240					87.4	0.6

[a] 2-Bromo-4-*tert*-butyltoluene, 3.8 ml (20 mmol); benzene, 7.1 ml (80 mmol); $AlCl_3$, 26.7 mg (0.2 mmol); T = 20 °C.

Other investigators[2,5,7] have reported that transfer of tertiary alkyl group from an aromatic hydrocarbon is accomplished with the soluble $AlCl_3$–CH_3NO_2 complex.

The results of our work show that no transalkylation takes place with the soluble $AlCl_3$–CH_3NO_2 or $AlCl_3$–Et_2O complexes even in large excess (150 mol %). Furthermore, no reaction takes place when a saturated solution of $AlCl_3$ in benzene (0.2% w/v[17]) is used as a catalyst. Addition of a small amount of solid $AlCl_3$ to this solution immediately promotes the transalkylation. The heterogeneity of the catalysis is depicted by the fact that the reaction proceeds only as long as solid $AlCl_3$ is present.

The influence of the catalyst's particle size and the incubation period (the time interval between mixing the catalyst with the acceptor and introducing the donor) on the reaction rate and induction period (Tables I and II) also indicates the heterogeneous nature of the catalyst. Two processes occur in the catalyst during the incubation period: (a) breakage of the particles; (b) dissolution (Table III). The result of the former is an increase of the catalyst's surface area while the latter decreases the amount of the active catalyst. Using a 300-μ particle size $AlCl_3$ an acceleration of the reaction rate is observed when the incubation period is increased up to 48 h,

Table III. Amount of Dissolved $AlCl_3$ in Benzene as a Function of Incubation Time

Incubation time, h	Liquid phase volume, ml	$AlCl_3$ introduced, mg	$AlCl_3$ dissolved, mg/ml	Total amount of $AlCl_3$ dissolved, mg
0.1	10.4	39.0	0.00	0.0
24	9.9	37.3	0.33	3.3
72	11.2	42.2	2.53	28.3
144	9.2	34.5	3.70	34.0

Table IV. Equilibrium Constants as a Function of the Temperature and ΔH in the Reaction between I as the Donor and Various Acceptors Catalyzed by $AlCl_3$

Acceptor	$K_{0°C}$	$K_{25°C}$	$K_{35°C}$	ΔH, kcal/mol
m-Xylene	0.26	0.26	0.27	+0.3 ± 0.3
Toluene	0.82	0.76	0.75	−0.3 ± 0.2
Benzene	2.91	2.14	1.84	−2.4 ± 0.4
Fluorobenzene	1.78	0.70	0.46	−6.9 ± 0.8
Chlorobenzene	4.10	1.54	1.00	−7.1 ± 0.7
Bromobenzene	5.31	1.78	1.12	−7.8 ± 0.7

Table V. Equilibrium Constants as a Function of the Temperature and ΔH in the Reaction between Various Donors and Benzene as Acceptors

Donor[a]	$K_{0°C}$	$K_{25°C}$	$K_{35°C}$	ΔH, kcal/mol
I	2.91	2.14	1.84	−2.4 ± 0.4
II	1.22	1.99	2.53	+3.8 ± 0.6
III	0.45	1.22	1.49	+5.1 ± 2.1
IV	3.45	2.27	2.08	−2.0 ± 0.3
V	8.93	4.53	3.67	−4.2 ± 0.3
VI	9.11	4.48	3.74	−4.0 ± 0.6

[a] Donors: I, 2-bromo-4-*tert*-butyltoluene; II, 2-bromo-4-*tert*-butylchlorobenzene; III, 1,2-dibromo-4-*tert*-butylbenzene; IV, 2-bromo-4-*tert*-butylethylbenzene; V, 1-bromo-2,6-dimethyl-3-*tert*-butylbenzene; VI, 2-bromo-1,6-dimethyl-4-*tert*-butylbenzene.

resulting from the increase of the catalyst's surface area. Longer incubation periods cause a decrease in reaction rate resulting from the reduction of the amount of active catalyst due to dissolution (Table II). No change in the reaction is observed with incubation periods up to 24 h when 50-μ (high surface area) particles are used. Longer incubation periods cause a decrease in reaction rate due to dissolution which decreases the amount of the solid catalyst (Table I).

The basicity of the bromo-substituted aromatic ring is lower than that of the hydrocarbon; hence a more acidic catalyst is needed to promote transalkylation in the case of the bromo-substituted compound. Any complexed $AlCl_3$ is a weaker Lewis acid than the uncomplexed salt.[18] This is the reason that complexed $AlCl_3$ catalyzes transalkylation from aromatic hydrocarbons[2,5,18] but a stronger catalyst like solid $AlCl_3$ is needed for transalkylation from brominated aromatic compounds.

It has been proved that after the reaction reaches a stage where no further change in the relative amounts of the reactants is observed, an equilibrium is reached. Addition of a new portion of reactants (after 1 h at equilibrium) causes the reaction to proceed until the initial equilibrium is reestablished. On the other hand, if the new portion of reactants is added after a long period (24 h) from the time the equilibrium is reached, the reaction does not proceed further, owing to deactivation of the catalyst.[19] At this stage a fatty brown layer

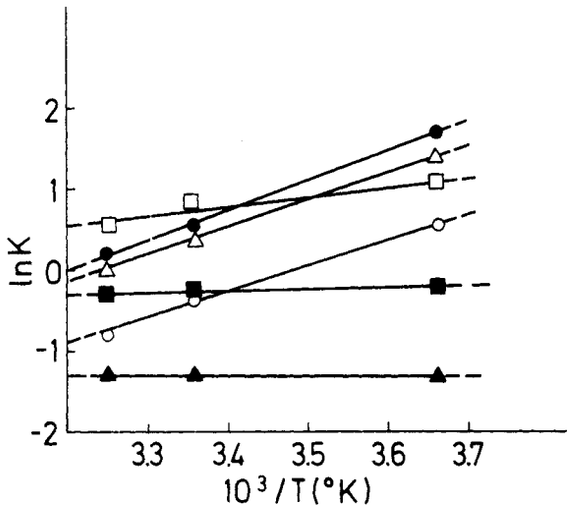


Figure 1. Ln K as a function of T^{-1} in the reaction between I as the donor and the following acceptors: ▲, m-xylene; △, chlorobenzene; ■, toluene; □, benzene; ●, bromobenzene; ○, fluorobenzene.

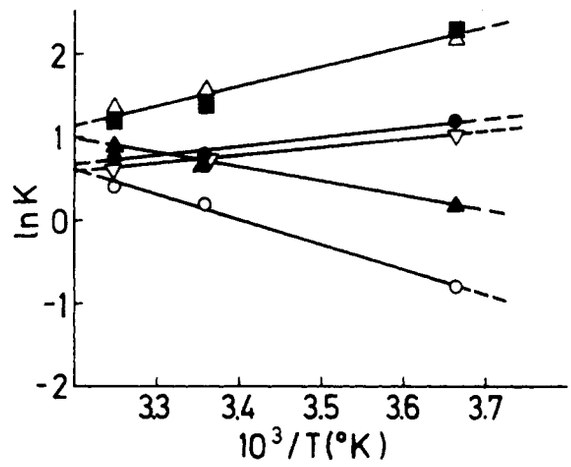


Figure 2. Ln K as a function of T^{-1} in the reaction between benzene as acceptor and the following donors: ▽, I; ▲, II; ○, III; ●, IV; ■, V; △, VI.

is separated from the reaction mixture.[19] Addition of another amount of solid catalyst reestablished the equilibrium.

Studying the reverse reaction (eq 1) with the same amount of catalyst shows that the reaction stops before it reaches equilibirum. Consecutive additions of small amounts of solid catalyst cause the reaction to continue until equilibrium is reached. Attempts to reach the equilibrium in one step, e.g., using a larger amount of solid catalyst, have been unsuccessful since side reactions (bromine migration) take place in addition to the desired transalkylation.

Equilibrium constants (K) and the calculated enthalpies of the reaction for different donor–acceptor systems are summarized in Tables IV and V.

Based on the calculated enthalpy of the reaction (Figure 1 and Table IV), it is possible to divide the acceptors into two major groups: (a) acceptors involved in reactions with low (+0.3 to −2.4) ΔH values, e.g., m-xylene, toluene, and benzene; (b) those involved in reactions showing relatively high (−6.9 to −7.8) values of ΔH, e.g., fluoro-, chloro-, and bromobenzene.

This behavior stems from the fact that the acceptor does not influence the rate of the forward reaction and is responsible only for the reverse process where it serves as a "donor". High-basicity acceptors (group a) facilitate the reverse reaction which results in low ΔH. The oppostie effect occurs with low-basicity acceptors (group b). Furthermore, the ΔH value in each group is increased with decreased basicity of the acceptor: (a) m-xylene < toluene < benzene; (b) fluorobenzene < chlorobenzene < bromobenzene. Similar results which strengthen the above explanation are obtained from the experiments with various donors and benzene as an acceptor (Table V and Figure 2). The above results are particularly important for choosing the proper reaction temperature for a given donor–acceptor system in synthetic applications of the process.

Experimental Section

Materials. Benzene was spectrograde Merck reagent dried over sodium emulsion and freshly distilled through a 2-ft column, at an atmospheric pressure, into a vessel containing sodium wires.

Other aromatic compounds were Fluka pure reagents dried over molecular sieve type 4A, activated at 400 °C.

Solution of $AlCl_3$ in nitromethane, 1 M concentration, was "Cationics" product used with no further treatment.

The donors were prepared as described in a previous paper.[1]

$AlCl_3$ was Fluka white resublimed solid of 99% purity. It was crushed and passed through appropriate sieves in a glove bag over P_2O_5, under dry nitrogen atmosphere, and immediately transferred into a dried 50-ml ground glass stoppered Erlenmeyer with a side arm covered by a rubber septum.

Transalkylation Reactions. $AlCl_3$ (26.7 mg, 0.2 mmol) and 7.1 ml (80 mmol) of benzene (introduced into the Erlenmeyer) kept in a drybox under dry N_2 were shaken together (for a predetermined incubation period); 3.8 ml of 2-bromo-4-*tert*-butyltoluene (20 mmol) was added by means of a syringe and the mixture was shaken at a constant temperature in a shaking bath. Samples (25 μl) were withdrawn (at predetermined reaction times) through the septum by means of a 25-μl syringe and quenched in 1 ml of diethyl ether containing 0.05 mmol of durene [used as a gas chromatograph (GLC) internal standard]. Transalkylations with other donors and acceptors were carried out following the same procedure.

For equilibrium constant determination the same procedure was used, with different ratios of reactants and catalyst. Solution of $AlCl_3$ in benzene was prepared by shaking a large excess of powdered $AlCl_3$ in benzene for 24 h, filtering the mixture through a 10-μ sintered glass funnel in a glove bag under dry nitrogen.

The soluble $AlCl_3$ content of the benzene solution and reaction mixtures was determined by means of a Perkin-Elmer Model 403 atomic absorption spectrophotometer using the following procedure: 1 ml of the $AlCl_3$ solution was extracted into a known volume of twice distilled water for Al^+ determination. For Cl^- determination a known volume of 0.1 N $AgNO_3$ solution was used to precipitate all the Cl^- present in 1.0 ml of $AlCl_3$ solution and the excess Ag^+ was determined.

In order to examine the accuracy of $AlCl_3$ analysis, a solid sample of 41.9 mg of $AlCl_3$ was analyzed following the above procedure. The obtained result was 41.5 ± 0.5 mg of $AlCl_3$.

For GLC analysis a Varian Aerograph gas chromatograph series 2800 with a thermal conductivity detector coupled to a Pantos Model u-125 recorder and an Autolab Model 6300 digital integrator was used.

Acknowledgment. The authors wish to thank Professor M. Levy of the Weizmann Institute of Science for his helpful remarks and Mrs. R. Bilu of the Casali Institute for atomic absorption determinations.

Registry No.—I, 61024-94-0; II, 61024-95-1; III, 6683-75-6; IV, 57190-08-6; V, 61024-96-2; VI, 61024-97-3; m-xylene, 108-38-3; toluene, 108-88-3; bromobenzene, 108-86-1; chlorobenzene, 108-90-7; benzene, 71-43-2; fluorobenzene, 462-06-6; $AlCl_3$, 7446-70-0; o-bromotoluene, 95-46-5.

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Concerning the Mechanism of Trimethylaluminum Addition to Benzophenone

E. C. Ashby* and R. Scott Smith

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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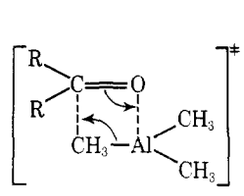
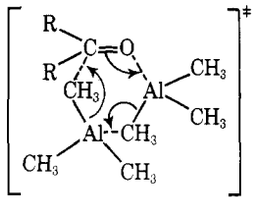
Because of the stereochemical significance of the reaction of $(CH_3)_3Al$ with substituted cyclohexanones in 2:1 ratio in benzene, an attempt was made to more clearly define the nature of the transition state involved in this reaction. In this connection, molecular weight and NMR studies were carried out on the systems $(CH_3)_3Al$–$O(C_2H_5)_2$, $(CH_3)_3Al$–$Ph_2C{=}O$, and $(CH_3)_2AlCl$–$Ph_2C{=}O$ in an attempt to distinguish among three suggested reaction pathways. One pathway involving the intermediate formation of two molecules of monomeric $(CH_3)_3Al$ bound to one molecule of $Ph_2C{=}O$ was eliminated by the data. All of the available data more strongly support a pathway involving cyclic six-center transition state.

The reaction between $(CH_3)_3Al$ and benzophenone in benzene is known to proceed by two distinct mechanistic pathways depending on the stoichiometric ratio of reactants.[1] At 1:1 ratio the reaction is first order in $(CH_3)_3Al$ and first order in ketone and is presumed to proceed via a four-center transition state (A) whereas in 2:1 ratio the reaction is second order in $(CH_3)_3Al$ and first order in ketone and is presumed to proceed via a six-center transition state (B). When the reaction is carried out in diethyl ether the kinetic order (first order in $(CH_3)_3Al$ and first order in ketone) is independent of the stoichiometric ratio of reactants and the mechanism has been represented as proceeding through transition state A.[2]



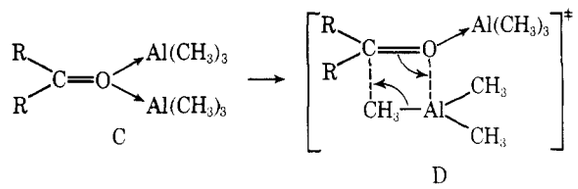
A



B

Since this reaction proceeds via two distinct mechanistic pathways in benzene and hence via two distinct transition states, it was presumed that the stereochemistry of the reaction at $(CH_3)_3Al$:ketone ratios of 1:1 and 2:1 would be different. In this connection, it was found that the reaction of $(CH_3)_3Al$ with 4-*tert*-butylcyclohexanone in 1:1 ratio in benzene resulted in 75% equatorial attack whereas the reaction in 2:1 ratio resulted in 90% axial attack. This is a rather dramatic and unprecedented stereochemical result and we have expended considerable effort in attempts to arrive at a satisfactory explanation.[3,4]

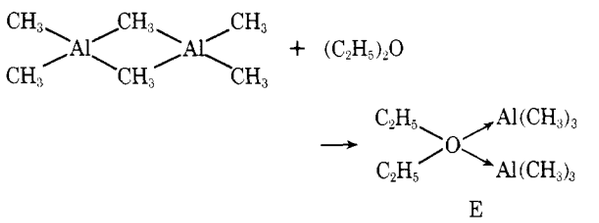
Recently, Kawasaki[5] has rationalized stereochemical data assuming transition state B and Starowieyski[6] has provided evidence for B by noting the stability of an acetophenone–$(AlCl_3)_2$ adduct. On the other hand, Mole[7] has suggested that the reaction in 2:1 ratio proceeds via the intermediate C leading to transition D. Because an understanding of the unusual stereochemical results of this reaction involving cyclohexanones necessitates an accurate picture of the transition state, we have set out to study the nature of the transition state involved in this reaction.



C D

Results and Discussion

If Mole is correct about the intermediacy of C, then it should be possible to detect such an intermediate spectroscopically (NMR) or by observing the colligative properties of the solutions on mixing $(CH_3)_3Al$ and $Ph_2C{=}O$ in 2:1 ratio in hydrocarbon solvent. We have approached this study in two ways. (1) substituting diethyl ether for $Ph_2C{=}O$ (we have shown comparable basicities of diethyl ether and $Ph_2C{=}O$ toward $(CH_3)_3Al$[3]), we should observe a structure comparable to C (e.g., E) when $(CH_3)_3Al$ and diethyl ether are allowed to react in 2:1 ratio provided that such a structure is present. Then (2) it should be possible to make a direct observation of C, provided that it is present in solution, by reaction of $(CH_3)_3Al$ and benzophenone in 2:1 ratio at sufficiently low temperatures where the addition reaction is very slow or nonexistent. Since the basicity of diethyl ether and benzophenone are approximately the same toward $(CH_3)_3Al$,[3] an analogy between the behavior of $(CH_3)_3Al$ and diethyl ether in 2:1 ratio and $(CH_3)_3Al$ and benzophenone in 2:1 ratio should



E (1)