Preparation of the Allyl Alcohol (24b). Treatment of Fp(*anti*-3-phenylallene) tetrafluoroborate (0.76 g, 2 mmol) as above with 21 mL of 0.1 N NaOH in acetone gave 0.10 g (16%) of the allyl alcohol (**24b**): IR (CH_2Cl_2) 3590, 2030, 1960 cm^{-1}; NMR (CS_2) δ 7.1–7.4 (m, 5, Ph), 5.94 (s, 1, =CH), 5.1 (s, 2, CH_2), 4.4 (s, 5, Cp). 1.65 (d, 1, J = 4 Hz, OH).

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (GP-27991), which are gratefully acknowledged.

Registry No.—**3**, 62685-81-8; **4**, 42065-40-7; 4 deuterium derivative, 66769-18-4; **5**, 66769-19-5; 5 deuterium derivative, 66769-20-8; **6**, 65097-84-9; **11**, 66769-21-9; **18**, 42043-77-6; **21a**, 66791-89-7; **21b**, 66791-90-0; **22a** deuterium derivative, 66769-22-0; **24b**, 66769-23-1; NaFp, 12152-20-4; 2-bromopropionaldehyde diethyl acetal, 3400-55-3; benzyltrimethylammonium acetate, 16969-11-2.

References and Notes

(1) A limited number of such complexes have been prepared either by metalation with the Fp anion of an α-halo ketone [J. K. P Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964)] or of an α-halo acetal [A. Cutler, S. Raghu, and M. Rosenblum, *J. Organomet. Chem.*, **77**, 381 (1974)].

(2) (a) P. Lennon, A. M. Rosan, and M. Rosenblum, *J. Am. Chem. Soc.*, **99**, 8426 (1977); (b) P. Lennon, M. Madhavarao, A. Rosan, and M. Rosenblum, *J. Organomet. Chem.*, **108**, 93 (1976); N. Genco, D. Marten, S. Raghu, and M. Rosenblum, *J. Am. Chem. Soc.*, **98**, 848 (1976); (c) A. M. Rosan and M. Rosenblum, *J. Org. Chem.*, **40**, 3621 (1975).

(3) B. Foxman, D. Marten, A. Rosan, S. Raghu, and M. Rosenblum, *J. Am. Chem. Soc.*, **99**, 2160 (1977).

(4) J. Benaim, J.-Y. Merour, and J.-L. Roustan, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 789 (1971).

(5) J.-L. Roustan and P. Cadiot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 734 (1969).

(6) S. Raghu and M. Rosenblum, *J. Am. Chem. Soc.*, **95**, 3060 (1973).

(7) D. W. Lichtenberg and A. Wojcicki, *J. Organomet. Chem.*, **94**, 311 (1975).

(8) C. J. Collins, *Carbonium Ions*, **1**, Chapter 9 (1968).

(9) P. W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88**, 5044 (1966).

(10) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A*, 1508 (1967).

(11) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).

(12) M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, **99**, 6099 (1977).

(13) M. D. Johnson and C. Mayle, *Chem. Commun.*, 192 (1969).

(14) A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Am. Chem. Soc.*, **98**, 3495 (1976).

(15) J.-Y. Merour and P. Cadiot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **271**, 83 (1970).

(16) D. Marten, private communication.

(17) B. L. Shaw and A. J. Stringer, *Inorg. Chim. Acta Rev.*, **7**, 1 (1973).

(18) B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 221 (1975).

(19) K. M. Nicholas and A.-M. Rosan, *J. Organomet. Chem.*, **84**, 351 (1975); A. Sanders, C. V. Magatti, and W. P. Giering, *J. Am. Chem. Soc.*, **96**, 1610 (1974).

(20) J. J. Eisch and R. B. King Ed., "Organometallic Synthesis", Vol. 1, Academic Press, New York, N.Y., p 114.

Specific Ortho Bromination of Substituted Benzenes. 3.[1a] Gas-Phase Dealkylation of the *tert*-Butyl Group from 4-*t*-Bu-2-BrC_6H_3X

David Meidar*[1b] and Yuval Halpern

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

Tuvia Sheradsky

Department of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received March 8, 1978

The use of solid acid catalyst for the gas-phase dealkylation of a *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X was studied. Reactions were carried out in a flow system in the temperature range of 250–400 °C at atmospheric pressure. The tendency of the bromine atom to cleave under the experimental conditions was followed. The lifetime of the catalyst was limited, but it could be reactivated easily. The advantages and limitations of the process are discussed.

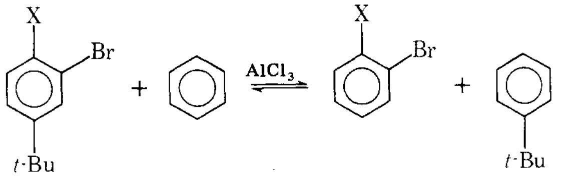
Introduction

Electrophilic aromatic substitution has been and still is being investigated, offering a large body of data including information on isomer distribution in the electrophilic substitution of substituted benzenes.[2] However, only a limited number of procedures for the selective introduction of a functional group into a substituted benzene using bulky positional protecting groups have been described earlier.[1,3-12] One of the bulk groups more frequently used as a positional protecting group is the *tert*-butyl group. In order to recover the final product, i.e., the 1,2-disubstituted aromatic compound, the *tert*-butyl group is usually removed by transfering it to another aromatic nucleus via a Friedel–Crafts type transalkylation reaction.[1,3-5,12] Catalysts for this reaction are generally based on aluminum chloride and related Lewis acid halides. However, this procedure requires an extensive separation technique due to the formation of a complex between the reactants and products with the catalyst as well as the formation of by-products.[12]

We now wish to report the easy and fast dealkylation of the *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X over an acidic solid catalyst in a continuous process.

Results and Discussion

In the course of our studies on the specific ortho bromination of substituted benzenes,[1,3,4] we found that the removal of the *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X to yield 2-BrC_6H_3X is achieved in the liquid phase by transalkylation reaction (eq 1), using $AlCl_3$ as catalyst, and excess benzene as solvent to shift the equilibrium composition to the right-hand side of eq 1.



(1)

X = CH_3, C_2H_5, Cl, Br

Although resulting in high yields and high isomer purity, the batch reaction is not convenient for preparation on a large scale. Since it is known that the *tert*-butyl group attached to an aromatic ring has a great tendency to cleave over solid acidic catalysts at elevated temperatures,[13] we investigated

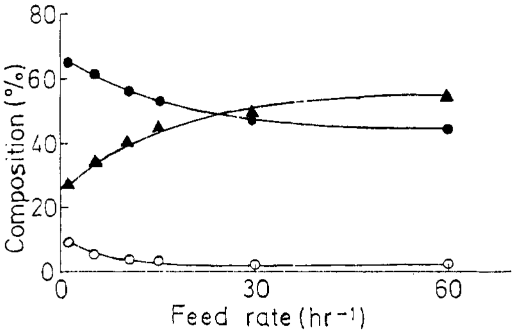
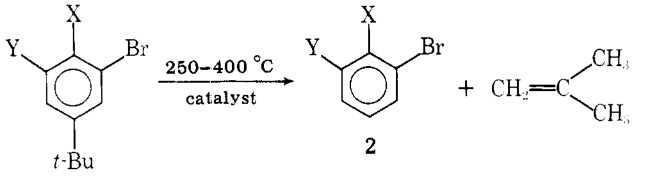


Figure 1. Composition of the reaction mixture after passing **1a** over SiO_2–Al_2O_3 at T = 350 °C at various feed rates (N_2 flow rate = 50 mL/min.): ●, *o*-bromotoluene; ▲, **1a**; ○, byproducts.

the cleavage of the *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X in the gas phase over solid acid catalyst (eq 2).



1 2 (2)

a, X = CH_3; Y = H
b, X = Cl; Y = H
c, X = Br; Y = H
d, X = C_2H_5; Y = H
e, X = CH_3; Y = CH_3

This process has the advantage of a flow system in which the used catalyst can be regenerated and no byproducts, except for isobutylene, are formed in the process. Thus, separation of the product from the unreacted precursor is very simple since the difference in boiling points of ArH and *t*-BuAr is in the range of 80 °C at atmospheric pressure. The recovered precursor can be recycled. Further, in liquid-phase transalkylation reactions, the Lewis acid catalyst must be quenched prior to distillation. The present process does not require any washing of the products, and the product mixture can be directly distilled.

As expected,[14] no dealkylation reactions took place when silica or alumina were used as the catalysts even at 450 °C. We did not use graphite-intercalated metal halides, which are known to rapidly decrease their activity during the process since active Lewis acid is leached out from the graphite.[15] On the other hand, an acid washed silica–alumina (7:1) catalyzed the gas-phase de-*tert*-butylation of **1a** to give **2a** in good conversions and excellent yields. The degree of conversion is dependent upon both the reaction time (Figure 1) and the temperature (Figure 2). Increasing both the temperature and the reaction time increases the degree of conversion.

Olah and Meyer investigated the effect of $AlCl_3$ on the isomerization of halotoluenes.[16] They found that fluorotoluenes and chlorotoluenes isomerize predominantly through intramolecular 1,2 shift. The observation of rearranged products containing as much as 20% chlorobenzene formed by disproportionation points to the methyl group as the migrating entity. In general, the isomerization rate was low at 100 °C, and increased in the order F > Cl. However, isomerization of bromotoluene was completed in ca. 30 min at ambient temperatures, giving the equilibrium isomers mixture. However, based on the data presented,[16] it could not be concluded whether the isomerization of *o*-, *m*-, and *p*-bromotoluenes proceeds through an intermolecular or an intramolecular mechanism.

Although silica–alumina is a much weaker acid than $AlCl_3$, we used elevated temperatures in which cleavage of the C–Br bond may occur even by the catalysis of an acid as weak as silica–alumina. Indeed, C–Br cleavage was observed yielding dibromotoluenes and toluene (eq 3) as well as *m*- and *p*-bromotoluene (eq 4).

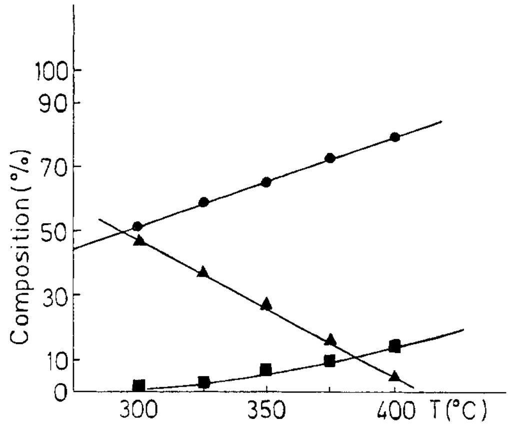
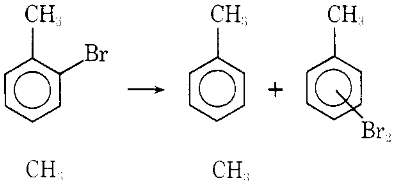
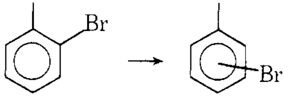


Figure 2. Composition of the reaction mixture after passing **1a** over SiO_2–Al_2O_3 at various temperatures (contact time = 1 s): ●, *o*-bromotoluene; ▲, **1a**; ■, byproducts.



(3)



(4)

While the intermolecular isomerization (eq 3) results in easily separated products, the intramolecular isomerization yields isomers which are difficult to separate. It has been observed that the extent of isomerization reactions increases when both the reaction time and temperature are increased. Table I summarizes selected de-*tert*-butylation data of **1a** to give **2a**. The data suggest that while the conversion and isomerization have the same qualitative dependence upon the temperature and the reaction time, the yield is scarcely affected by these parameters.

When transalkylation reactions were carried out in the liquid phase, and catalyzed by water-promoted Lewis acids, it was shown[17] that the reaction rate was dependent upon the basicity of **1**. The more basic **1** is, the higher the reaction rate. Moreover, measurement of $\Delta H^{\ddagger}$ revealed that the more basic **1** is, the lower $\Delta H^{\ddagger}$, i.e., the less temperature dependent is the reaction rate.

Since both the liquid-phase transalkylation and the gas-phase dealkylation are catalyzed by the same species, i.e., the proton, the behavior of **1** over silica–alumina was expected to be similar to that of **1** in a liquid-phase system containing water-promoted Lewis acids. Figure 3 shows good agreement with this expectation. The most basic, **1e**, gives the highest conversion with the least dependence upon temperature while the least basic, **1c**, gives the lowest conversion with the highest temperature dependence.

Alkenes are well known poisons for many solid catalysts as they tend to polymerize on the catalyst surface. In the present experiments, measurements show a gradual decrease of the conversion as the onstream time increased (Figure 4). This decrease in the catalyst activity is attributed to polymerization of the isobutylene formed in the process. The extent of decrease in activity varies, depending upon the temperature and the reaction time. However, the catalyst can be regenerated

Table I. Yields and Purities of *o*-Bromotoluene Obtained by the Dealkylation of 1a over SiO_2–Al_2O_3 at Various Reaction Conditions

T, °C	contact time, s	feed rate, h^{-1}	% conversion	% recovery of precursor	% purity of ortho isomer
350	0.2[a]	60	45	53	>99.5
300	1.0[b]	1.1	51	48	99.5
325	1.0[b]	1.1	60	35	99.0
350	0.4[a]	30	48	50	99.0
350	0.8[a]	15	53	43	98.7
400	0.2[a]	60	51	46	98.5
350	1.2[a]	10	56	40	98.2
400	0.4[a]	30	54	42	98.2
350	1.0[b]	1.1	65	28	98.0
350	2.5[a]	5	60	35	97.5
375	1.0[b]	1.1	73	17	97.0
400	1.0[b]	1.1	80	5	96.5

[a] Nitrogen flow rate = 50 mL/min. [b] Nitrogen flow rate = 400 mL/min.

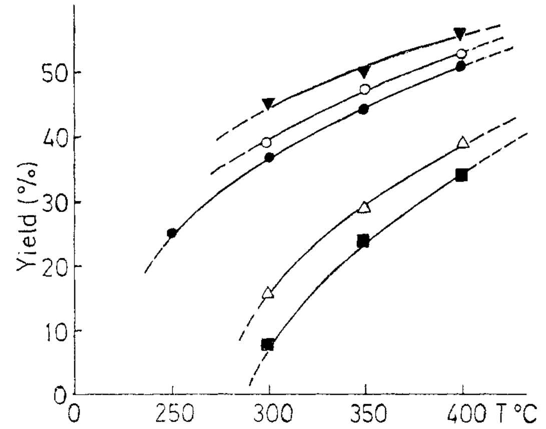


Figure 3. Percent conversion of ortho bromo-substituted benzenes on passing 1a–1e over SiO_2–Al_2O_3 at various temperatures (contact time = 0.2 s): ●, **1a**; △, **1b**; ■, **1c**; ○, **1d**; ▼, **1e**.

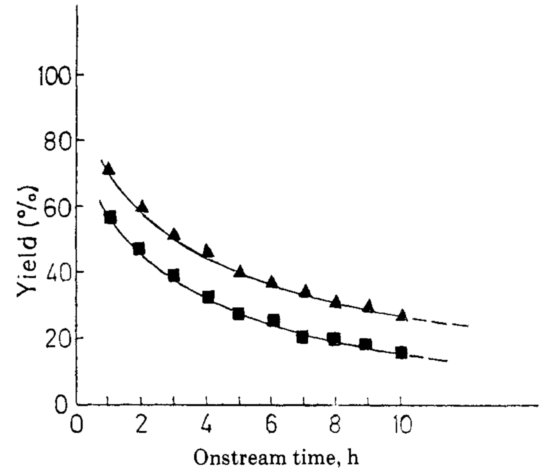


Figure 4. Catalytic activity (% conversion) of SiO_2–Al_2O_3 as a function of the onstream time. T = 350 °C; contact time = 0.2 s: ▲, over fresh catalyst; ■, over reactivated catalyst.

to ca. 80% of its original reactivity by heating it to 500 °C in an air stream.

Conclusion

The present process provides a simple method for the removal of the blocking group, namely, the *tert*-butyl group. Yield is excellent in this process with ca. 50% conversion. Workup requires only separation by distillation after which the unreacted precursor can be recycled.

Experimental Section

Reagents. All starting materials were prepared as described previously.[3]

Experimental Procedure. Gas-phase reactions over SiO_2–Al_2O_3 (7:1) were carried out in a 210 × 11.3 mm glass tube reactor in which the catalyst was supported by glass wool. The reactor was charged with 8.6 g (15 mL) of the solid catalyst, while dry N_2 was passed through at rates of 50 and 400 mL/min. The reactor was electrically heated to a predetermined temperature (temperature deviation was ±2 °C). Products emerging from the catalytic reactor were condensed and analyzed by gas–liquid chromatography. Under the experimental conditions used, the space velocity was in the range of 9.2×10^{-5} to 1.7×10^{-6} mol/s g of catalyst, and the contact time over the catalyst was 0.2–2.5 s.

Analysis of Products. Products were analyzed by gas–liquid chromatography using a Varian gas chromatograph Model 2800 equipped with thermal conductivity detector. A 3 ft × 1/8 in. 10% SE-30 on gas Chromosorb P column was used to analyze reaction mixtures. For isomer analysis a 10 ft × 1/8 in. 3% XE-60 on gas Chromosorb P column separated ortho isomer from meta and para isomers. Peak areas were integrated using an Autolab digital integrator Model 6300.

Acknowledgment. The authors wish to thank Professor George A. Olah of the University of Southern California for his helpful remarks.

Registry No.—**1a**, 61024-94-0; **1b**, 61024-95-1; **1c**, 6683-75-6; **1d**, 57190-08-6; **1e**, 61024-97-3; **2a**, 95-46-5.

References and Notes

(1) (a) For part 2, see: Y. Halpern and D. Meidar, *J. Org. Chem.*, **42**, 422 (1977). (b) Department of Chemistry, University of Southern California, University Park, Los Angeles, Calif. 90007.
(2) D. Meidar and Y. Halpern, *J. Appl. Chem. Biotechnol.*, **26**, 590 (1976).
(3) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions", Vol. II, Wiley-Interscience, New York, N.Y., 1964.
(4) Y. Halpern and D. Meidar, *Org. Prep. Proced. Int.*, **8**, 299 (1976).
(5) M. J. Schlatter, *J. Am. Chem. Soc.*, **76**, 4952 (1954).
(6) F. R. J. Willemse, J. Walters, and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **90**, 5 (1971).
(7) F. R. J. Willemse, J. Walters, and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **90**, 14 (1971).
(8) N. Yoneda, M. Tashiro, and H. Ohtsuka, *Nippon Kagaku Kayshi*, 331 (1973).
(9) Y. Mite and N. Kametake, *Hydrocarbon Process.*, **47**, 122 (1968).
(10) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **35**, 3717 (1970).
(11) V. N. Ipatieff and B. B. Carson, *J. Am. Chem. Soc.*, **59**, 1417 (1937).
(12) M. Tashiro and G. Fukata, *Org. Prep. Proced. Int.*, **8**, 52 (1976).
(13) Khr. Dimitrov, Z. Popova, Tsv. Obretenov, G. Rangelov, and V. Mandova, *God. Sofii Univ., Khim. Fak. 1968–1969*, **63**, 55 (1971); *Chem. Abstr.*, **77**, 164278 (1971).
(14) C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1964).
(15) G. A. Olah, J. Kaspi, and J. Bukala, *J. Org. Chem.*, **42**, 4187 (1977).
(16) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962).
(17) D. Meidar and Y. Halpern, "Specific Ortho Bromination", Part 4, in preparation.