benzenes for nmr studies were prepared by adding 0.2 g of the fluorobenzene to 2 ml of SbF_5-HF-SO_2ClF solution which had been cooled at −78°. Upon warming and stirring, clear solutions were obtained.

Nmr Studies.—A Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe was used to obtain all spectra. Capillary TMS and $CFCl_3$ were used for proton and fluorine references, respectively.

Kinetic Analysis.—The activation energies for intramolecular 1,2-hydrogen shifts in protonated *o*-difluorobenzenes were determined by nmr line shape analysis. A computer stimulation of line shape was employed based on the Gutowsky-Holm[11] equation for multiple-site exchange. Activation parameters were calculated as previously described.[1b]

All the temperature-dependent nmr spectra are reversible under the studied conditions, unless otherwise mentioned.

Acknowledgment.—Support of our work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

Notes

Stable Carbocations. CLVI. Dealkylative Formation of the *tert*-Butyl Cation from Substituted *tert*-Butylbenzenes with Fluoroantimonic Acid[1]

GEORGE A. OLAH AND Y. K. MO

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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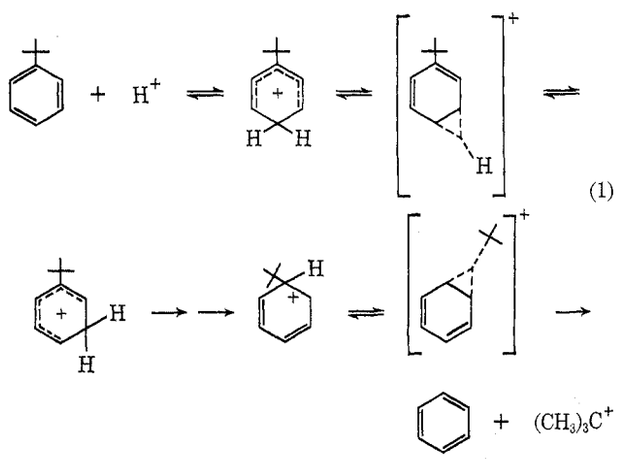
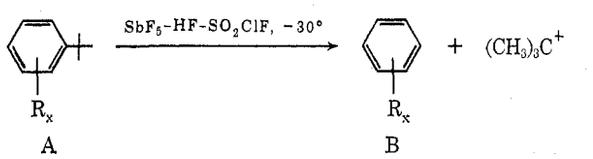
Under Friedel–Crafts reaction conditions, isomerization of di-*tert*-butylbenzene[2] and *tert*-butyltoluene[3] is well known. Under stable ion conditions, isomerization processes of alkylbenzenium ions[4] were also studied. In the study of protonation of alkylbenzenes, *tert*-butylbenzene was found to cleave readily to benzene and *tert*-butyl cation in superacid media even at low temperature.[4,5] The study of protonation of *tert*-butylbenzene in superacids at low temperature also provided direct experimental evidence for the formation of the *tert*-butylbenzenium ion. Raising the temperature results in intramolecular hydrogen migration as is shown by temperature-dependent nmr spectra. Eventually, the proton is attached to the carbon carrying the *tert*-butyl group (in all probability) and subsequently the *tert*-butyl cation is cleaved according to an α,β-cleavage mechanism (eq 1).



(1)

Ring-substituted alkylbenzenes, particularly with electron-withdrawing or sterically crowded groups, make formation of ring-protonated arenium ions increasingly difficult or even prevent it. In order to gain further insight into the protolytic behavior of *tert*-butylbenzenes with increasing substitution, we studied 17 substituted *tert*-butylbenzenes in SbF_5–HF–SO_2ClF solution at −30°. In all cases, *tert*-butyl cation was formed as evidenced by its pmr singlet absorption[2] at δ 4.0–4.2 (dependent on concentration and media). This peak was increased in intensity by adding a known solution of the *tert*-butyl cation. The pmr spectra of



A B

R_x = F_5, *o*-F, *p*-F, *p*-NH_2, *m*-$CONH_2$, *o*-, *p*-NO_2, *p*-$COCH_3$, *p*-COOH, *o*-, *m*-, *p*-*tert*-butyl, 3,5-di-*tert*-butyl, 3,5-di-*tert*-butyl-4-nitro, 3,5-di-*tert*-butyl-4-bromo, 2,4,5- and 3,4,5-tri-*tert*-butyl

the de-*tert*-butylated benzenes are identical with those of the corresponding benzenes derivatives in the same superacid media. For example, the pmr spectrum of *p*-*tert*-butylbenzoic acid in SbF_5–HF–SO_2ClF solution is identical with that of the *tert*-butyl cation and O-protonated benzoic acid in the same superacid solution.

Owing to the electron-withdrawing groups (*e.g.*, F_5, COOH, and NO_2), protonation at ring and subsequent benzenium–benzonium–benzenium ion rearrangement leading to cleavage of the *tert*-butyl group may not be necessary. Protonation may directly involve the C_{Ar}–C_α bond *via* a three-center bonded transition state (I) (thus reacting in accordance with known protolytic behavior of neopentane derivatives).

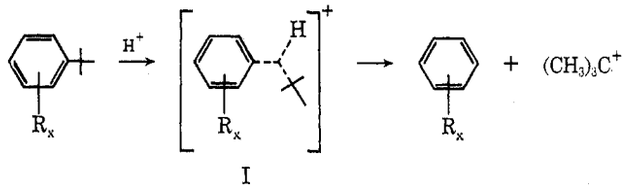
(1) Part CLV: G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3387 (1973).

(2) G. A. Olah, C. G. Carlson, and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964).

(3) G. A. Olah, N. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2310 (1964).

(4) For a review and references see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 865.

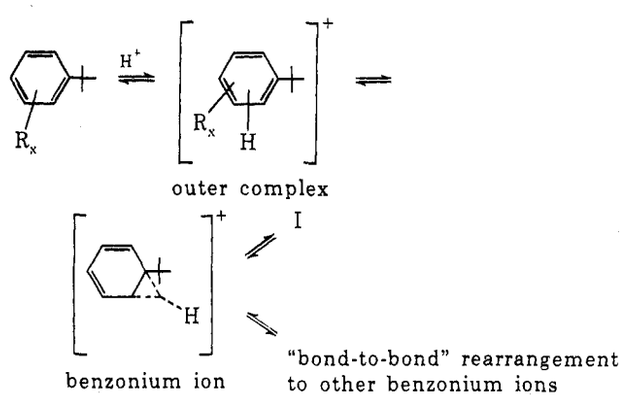
(5) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972), and references cited therein.



I

R_x are deactivating groups

Alternatively, initial interaction of the protonating agent with the deactivated or sterically crowded ring could form an outer complex[6] in equilibrium with an oriented π complex (benzonium ion[7]), then undergo intramolecular "bond-to-bond" rearrangement[8] and lead to the formation of I.



outer complex

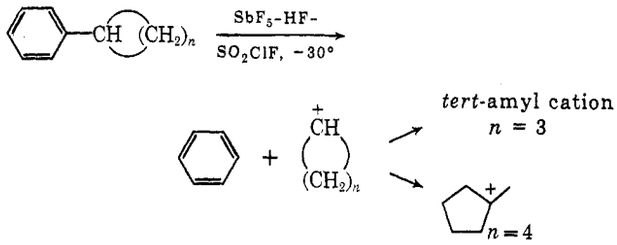
benzonium ion

"bond-to-bond" rearrangement to other benzonium ions

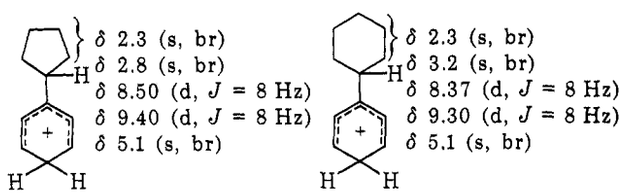
Our proposed mechanism is based on the fact that the formation of σ complexes (benzenium ions) in these systems is difficult or even does not take place. For example, we recently studied the protonation of pentafluorotoluene in superacid media and found no ring protonation.[9] Indeed, pentafluorotoluene underwent protolytic cleavage in superacids to give pentafluorobenzyl cation, $C_6F_5CH_2^+$, and H_2. Thus, the protolytic cleavage of pentafluoro-*tert*-butylbenzene in superacid to give *tert*-butyl cation and pentafluorobenzene may not involve any ring protonation. In other cases [$XC_6H_4C(CH_3)_3$, X = NO_2, COOH, $COCH_3$, NH_2, etc.], protonation may proceed at the n-donor side chain sites in preference to the π-donor ring. The corresponding benzenium ions (σ complexes) of these deactivated benzenes were never directly observed. Consequently, we conclude that dealkylation of these deactivated *tert*-butylbenzenes may also not involve any ring protonation prior to C_{Ar}–C_α bond protolysis.

Poly-*tert*-butylbenzenes such as 1,2,4,5- and 1,3,4,5-tetra-*tert*-butylbenzenes also cleaved to benzene and the *tert*-butyl cation in fluoroantimonic acid. As initial benzenium ion formation in these sterically crowded systems is unfavorable, protolytic cleavage may involve similar σ-bond reactivity as in the case of deactivated *tert*-butylbenzenes.

Cyclopentyl- and cyclohexylbenzenes behave very much as tertiary alkylbenzenes when treated with SbF_5–HF–SO_2ClF solution at −30°. Protolytic C_{Ar}–C_α bond cleavage takes place forming, besides benzene, *tert*-amyl and methylcyclopentyl cations, respectively. Under these conditions, the initially formed cyclohexyl



and cyclopentyl cations are known to rearrange to give methylcyclopentyl and *tert*-amyl cations, respectively.[10] The driving force for C_{Ar}–C_α over C_α–H protolysis (the corresponding 1-methyl-1-cyclopentyl cation is a known very stable ion) must be the higher reactivity of the C–C bond. The initial protonation in cycloalkylbenzenes is on the aromatic ring, as they can be protonated in superacid at −78° to give the stable cycloalkylbenzenium ions. The pmr spectra of the ions are in accordance with their structures.



In conclusion, our study on dealkylation of substituted *tert*-butylbenzenes under stable ion conditions proves that *tert*-alkylcarbenium ions are indeed involved in Friedel–Crafts isomerization of alkylbenzenes.

Experimental Section

Materials.—All the substituted *tert*-butylbenzenes were either commercially available materials (Aldrich Chemical Co.) or prepared according to the literature. Cyclopentyl- and cyclohexylbenzenes were obtained from Aldrich Chemical Co. Antimony pentafluoride (Allied Chemical Co.) was triply distilled before used. HF was obtained from J. T. Baker Chemical Co. The preparation of anhydrous fluoroantimonic acid has been described previously.[11] Spectrograde $HSbF_6$ was obtained from Cationics Inc.

Dealkylation of Substituted *tert*-Butylbenzenes with Fluoroantimonic Acid.—HF–SbF_5 (1.5 ml) was diluted with an equal volume of sulfuryl chloride fluoride (SO_2ClF) at −78°. To the resulting cold solution was added with vigorous stirring the substituted *tert*-butylbenzene (*ca.* 0.2 ml, 0.2 g) at −30°. The clear solution which formed was transferred to an nmr tube for spectral studies.

Ions not described in detail (pmr spectra) in this paper were already reported and characterized in our previous studies.

Nmr spectra were obtained on a Varian A-56-60A nmr spectrometer equipped with a variable-temperature probe. Chemical shifts are referred to external capillary TMS.

Acknowledgment.—The support of our work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No.—A (R_x = F_5), 40782-24-9; A (R_x = *o*-F), 320-11-6; A (R_x = *p*-F), 701-30-4; A (R_x = *p*-NH_2), 769-92-6; A (R_x = *m*-$CONH_2$), 40782-26-1; A (R_x = *o*-NO_2), 1886-57-3; A (R_x = *p*-NO_2), 3282-56-2; A (R_x = *p*-$COCH_3$), 943-27-1; A (R_x = *p*-COOH), 98-73-7; A (R_x = *o*-*tert*-butyl), 1012-76-6; A (R_x = *m*-*tert*-butyl), 1014-60-4; A (R_x = *p*-*tert*-butyl), 1012-72-2; A (R_x = 3,5-di-*tert*-butyl), 1460-02-2; A (R_x = 3,5-di-

(6) Using Mulliken's definition: R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 600 (1950); *J. Phys. Chem.*, **56**, 801 (1952).
(7) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971).
(8) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).
(9) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.
(10) (a) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2692 (1967); (b) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).
(11) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).

tert-butyl-4-nitro), 4074-25-3; A (R_x = 3,5-di-*tert*-butyl-4-bromo), 3975-77-7; A (R_x = 2,4,5-tri-*tert*-butyl), 796-97-4; A (R_x = 3,4,5-tri-*tert*-butyl), 40782-30-7; B (R_x = F_5), 363-72-4; B (R_x = F), 462-06-6; B (R_x = NH_2), 62-53-3; B (R_x = $CONH_2$), 55-21-0; B (R_x = NO_2), 98-95-3; B (R_x = $COCH_3$), 98-86-2; B (R_x = COOH), 65-85-0; B (R_x = *tert*-butyl), 98-06-6; B (R_x = *m*-di-*tert*-butyl), 1014-60-4; B (R_x = 1,3-di-*tert*-butyl-2-nitro), 15141-43-2; B (R_x = 1,3-di-*tert*-butyl-2-bromo), 19715-32-3; B (R_x = 1,2,4-tri-*tert*-butyl), 1459-11-6; B (R_x = 1,2,3-tri-*tert*-butyl), 40782-34-1; *tert*-butyl cation, 14804-25-2.

Cleavage of Allyloxycarbonyl Protecting Group from Oxygen and Nitrogen under Mild Conditions by Nickel Carbonyl

E. J. COREY* AND J. WILLIAM SUGGS

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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This note outlines a method for the use of the allyloxycarbonyl group for protection of hydroxyl and amino functions.

Allyl and cinnamyl acetates have been reported to react with nickel carbonyl at 45–65° in tetrahydrofuran for 2–3 hr to form the allylic coupling products (1,5-hexadienes) in 30–50% yield.[1] Under these conditions nonallylic acetates and allylic alcohols or ethers are unreactive. These facts suggest that the allyloxycarbonyl group could be used for hydroxyl or amino protection in a way parallel to the well-known benzyloxycarbonyl (carbobenzoxy) group and removed under mild aprotic conditions by the action of nickel carbonyl or a related "allylophilic" reagent. Experimental verification of this possibility was readily obtained. The conversion of a variety of alcohols to alkyl (or cycloalkyl) allyl carbonates could be accomplished in high yield by reaction with allyl chloroformate (available from Polysciences, Inc., Warrington, Pa.) and pyridine in a suitable aprotic solvent [*e.g.*, ether or tetrahydrofuran (THF)]. Regeneration of alcohol from the corresponding alkyl allyl carbonate occurred upon exposure to nickel carbonyl, as expected, but it was found that the reaction could not be driven to completion even with an excess of the reagent. This difficulty could be overcome by the addition of *N,N'*-tetramethylethylenediamine to reaction mixtures in either acetonitrile or dimethylformamide (DMF) as solvent, although an excess of nickel carbonyl was found still to be necessary.[2] For optimal yields of alcohols from alkyl allyl carbonates, the following reaction conditions were typically employed: (a) *ca.* 5 equiv of nickel carbonyl and 3 equiv of tetramethylethylenediamine per equiv of allyl carbonate, (b) DMF [5–10 ml/ml of $Ni(CO)_4$] as solvent at 55°, (c) nitrogen or argon atmosphere, (d) *ca.* 4 hr reaction time. Under these quite mild conditions the following cleavages of alkyl allyl carbonates to alcohols were observed (yield in parentheses).

$$\text{ROCOOCH}_2\text{CH=CH}_2 \xrightarrow{\text{Ni(CO)}_4} \text{ROH}$$

R = *n*-decyl (95%)
R = *exo*-2-norbornyl (87%)
R = menthyl (91.5%)

To illustrate the use of the allyloxycarbonyl group for protection of amino nitrogen, two substrates, *N*-allyloxycarbonyl-*dl*-phenylalanine[3] and *N*-allyloxydicyclohexylamine, were prepared and treated with nickel carbonyl under the conditions outlined above except for the use of DMF–water (95:5) as medium and 10 equiv of nickel carbonyl. The expected free amino compounds, *dl*-phenylalanine and *N,N*-dicyclohexylamine, were obtained in 95 and 83% yield.

We expect that for large-scale preparative work where the use of excess nickel carbonyl may be unacceptable, the use of a carbon monoxide atmosphere under pressure is advisable to stabilize the reagent.

Experimental Section

The following procedures for the synthesis and cleavage of the allyloxycarbonyl derivative of 1-decanol could also be applied to *exo*-2-norborneol and menthol.

Decyl Allyl Carbonate.—A magnetically stirred solution of 1-decanol (3.24 g, 20.5 mmol) and pyridine (2.03 g, 25.7 mmol) in 75 ml of THF was cooled to 0°, and allyl chloroformate (3.097 g, 25.7 mmol) in 10 ml of THF was added dropwise. The reaction mixture was slowly warmed to room temperature, and after 2 hr at room temperature the solution was filtered and solvent was removed at reduced pressure. Ether (25 ml) was then added and the solution was filtered again, washed with water and brine, dried over anhydrous $MgSO_4$, then distilled to give 4.54 g (91%) of a pleasant-smelling liquid: bp 109–110° (0.5 mm); ir (neat) 1751 (s), 1647 (w), 1292 (sh), 1250 (s, b), 970 (m), 795 cm^{-1} (m); nmr (CCl_4) δ 6.34–5.70 (9-line multiplet, 1 H), 5.37 (ABC triplet, 2 H), 4.61 (d, J = 5 Hz, 2 H) (these three absorbances are due to the allyl group and are the same in all the carboallyloxy derivatives made), 4.14 (t, J = 6 Hz, 2 H), 1.33 (s, 16 H), 0.97 (m, 3 H); mass spectrum m/e 140 [$(CH_2)_{10}^+$].

1-Decanol.—(Nickel carbonyl is both volatile and toxic; all operations involving it were performed in a well-ventilated hood.) Into a 25-ml flask fitted with a side arm and reflux condenser topped by a three-way stopcock opened to an argon-filled balloon were placed *n*-decyl allyl carbonate (0.288 g, 1.19 mmol), tetramethylethylenediamine (0.417 g, 3.60 mmol), and 7 ml of dry, argon-saturated DMF. Nickel carbonyl (0.78 ml, 6.0 mmol) was added all at once, and the stirred mixture was warmed slowly to 55°. After 4 hr excess nickel carbonyl was removed by codistillation with ether into an ethereal iodine solution. The mixture was poured into 20 ml of water and extracted twice with 15 ml of pentane. The pentane layer was washed with 20 ml of 1 *N* hydrochloric acid and brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent at reduced pressure gave 0.177 g (95%) of 1-decanol, homogeneous by tlc and with spectral properties identical with those of authentic material.

Cleavage of Allyloxycarbonyl Amides. A. *N*-Allyloxycarbonyl-*N,N*-dicyclohexylamine.—The above procedure was followed except that 0.3 ml of water was also added to the reaction mixture, and 10 equiv of nickel carbonyl was used. After removal of excess nickel carbonyl, the reaction mixture was poured into 20 ml of 1 *N* HCl, and the solution was made basic with sodium carbonate and extracted thrice with pentane. These pentane extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give dicyclohexylamine (95% yield).

B. *N*-Allyloxycarbonyl-*dl*-phenylalanine.—The reaction conditions were as described just above. After 5 hr excess nickel carbonyl and TMEDA were removed under reduced pressure. Then 50 ml of water was added and H_2S was bubbled through the solution for 10 min. The solution was brought to pH 6, heated

(1) N. L. Bauld, *Tetrahedron Lett.*, 859 (1962).

(2) The role of tetramethylethylenediamine in this regard is unclear. It was originally considered that the formation of Ni(II) as a reaction product might somehow inhibit the reaction and that the diamine might prevent such inhibition by complexation. However, it has been observed that added nickel acetate has no effect on the rate or extent of reaction between alkyl allyl carbonate and nickel carbonyl alone.

(3) C. M. Stevens and R. Watanabe, *J. Amer. Chem. Soc.*, **72**, 725 (1950).