Tetrahedron Letters No. 39, pp.3575 - 3578, 1971. Pergamon Press. Printed in Great Britain.

ACID-CATALYZED REARRANGEMENTS IN A CROWDED AROMATIC SYSTEM

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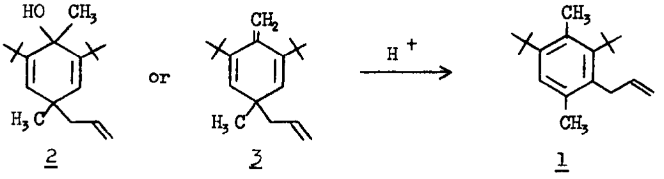
(Received in US 12 July 1971; received in UK for publication 27 August 1971)

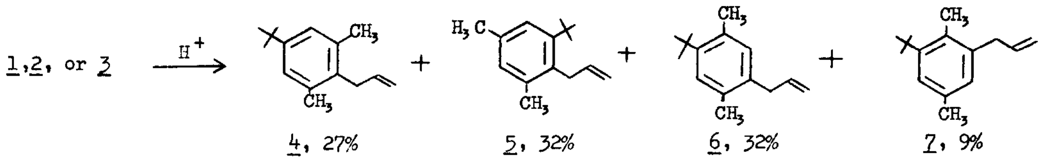
The presence of a *t*-butyl group *ortho* to another substituent on an aromatic ring causes appreciable steric strain in the molecule. The strain energy in *o*-*t*-butyltoluene has been estimated to be around 4-6 kcal./mole,[1,2] while the presence of a second methyl group *ortho* to the *t*-butyl group in 2,6-dimethyl-*t*-butylbenzene has been estimated to raise the strain energy to 17.6-24 kcal./mole.[2,3] Such crowding should increase the driving force for migration of substituents to other positions on the ring. Olah and his co-workers have investigated the aluminum chloride catalyzed rearrangements of *o*-*t*-butyltoluene [4] and *o*-di-*t*-butylbenzene.[5] These rearrangements proceeded rapidly to give the *para*-substituted isomers, together with products resulting from intermolecular transalkylation reactions. The rearrangements appeared to proceed principally by formation of *t*-butyl carbonium ions, which then realkylated the aromatic rings.[4,5] Some evidence for a competing 1,2 shift in the rearrangement of *o*-*t*-butyltoluene was presented,[4] although in this compound it cannot be determined which group undergoes any such shift.

We now wish to report our observations on the acid-catalyzed rearrangements of the very crowded molecule 1-allyl-2,4-di-*t*-butyl-3,6-dimethylbenzene (1).

Reaction of either the dienol 2 or the semibenzene 3 with a 1% solution of sulfuric acid in acetic acid for ten minutes gave a 97% yield of the "normal" allyl migration product 1.



(1)



(2)

TABLE

Nmr Spectra in CCl_4
(Chemical Shifts in Units of τ)

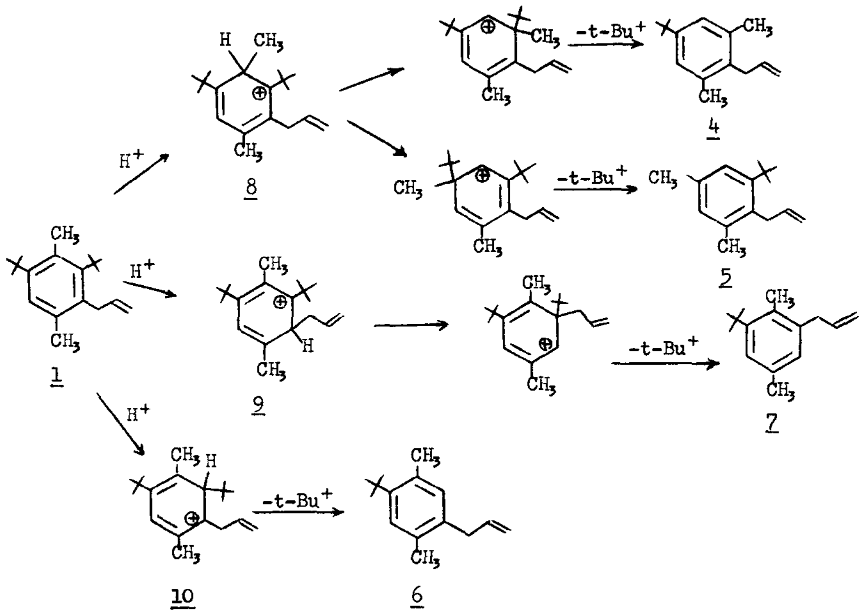
Cmpd.	t-Bu (s)	Ar-CH_3 (s)	Ar-CH_2-CH=CH_2 (m)	Ar-H
1	8.52 (9H) 8.60 (9H)	7.44 (3H) 7.85 (3H)	6.43	3.13 (s,1H)
4	8.72 (9H)	7.77 (6H)	6.70	3.13 (s,2H)
5	8.62 (9H)	7.78 (3H) 7.82 (3H)	6.43	3.07 (d,J=1,1H) 3.28 (d,J=1,1H)
6	8.62 (9H)	7.57 (3H) 7.82 (3H)	6.77	3.06 (s, 1H) 3.25 (s, 1H)
7	8.62 (9H)	7.62 (3H) 7.77 (3H)	6.72	3.07 (d,J=1,1H) 3.27 (d,J=1,1H)

s=singlet, d=doublet, m=multiplet

Rearrangement of 1,2, or 3 in a 10% solution of sulfuric acid in acetic acid for 20 hours gave identical mixtures of four products from the three starting materials. The products were identified as hydrocarbons 4-7, largely on the basis of spectroscopic evidence. The yield of each product is shown in equation (2).

The nmr spectra of the products obtained from reactions (1) and (2) are summarized in the Table. Perhaps the most informative features of these spectra are the downfield shifts of protons adjacent to t-butyl groups. Thus, aromatic protons *ortho* to t-butyl groups appear around τ 3.1, while those in other positions appear upfield near τ 3.3. Similarly the resonances for methylene and methyl groups *ortho* to t-butyl groups appear ca. 0.2 to 0.3 τ units downfield from those in other positions. These observations are in accord with previous observations on the effects of t-butyl substitution on the positions of nmr peaks for substituents on aromatic rings.[6,7] Taken together with the evidence for molecular symmetry in the spectrum of compound 4, and the *meta* coupling exhibited by the aromatic protons in 5 and 7, the positions of the peaks in the nmr spectra uniquely define the structures of these molecules.

Clearly, the major rearrangement processes involved in formation of compounds 4-7 from 1 involve migration of methyl groups, rather than t-butyl or allyl groups. It would be difficult to conceive of any of these products arising by intermolecular processes. The simplest mechanisms for these migrations are outlined in the scheme below.



The surprising conclusion that the predominant reaction is migration of the poorest migrating group, a methyl group, can be rationalized by the assumption that the initial protonation occurs predominantly on the carbon atom flanked by the t-butyl groups, to give carbonium ion 8. Indeed , the extent of protonation to form 8 seems likely to be even greater than that indicated by the amount of 4 and 5 formed, since migration of an allyl group or loss of a t-butyl group should intrinsically be faster processes than migration of methyl groups. If carbonium ions 8-10 are in equilibrium, therefore, a calculation from the yields of 6 and 7 would tend to exaggerate the amount of 9 and 10 in the equilibrium mixture.

Protonation of 1 at the most hindered position on the ring seems, at first glance, to be quite improbable. However, inspection of molecular models demonstrates clearly that formation of carbonium ion 8 should be the most favorable protonation process, since the strain caused by steric interference of the two t-butyl groups with the methyl group between them is relieved when the methyl group is moved out of the plane in which the t-butyl groups lie.

Similarly, protonation at a carbon atom bearing a t-butyl group occurs solely at the position between the methyl and allyl groups, rather than at the position ortho only to a methyl group. Again, this can easily be explained on steric grounds, since protonation to form carbonium ion 10 will move the t-butyl group out of the plane bearing the adjacent methyl and allyl groups. Clearly, this would result in greater relief of steric strain than would protonation at the carbon bearing the other t-butyl group.

Attempts to predict the direction of migration of a methyl group in carbonium ion 8 lead to ambiguous results. Migration of a methyl toward the allyl group will move the t-butyl group of the plane of the allyl group, but would place both a methyl and a t-butyl group on the carbon atom *ortho* to that bearing the allyl group. It is not clear whether this would result in formation of a more strained carbonium ion than that which would be formed by migration of a methyl to the carbon bearing the other t-butyl group. It is interesting that almost equal amounts of the two types of migration occur.

Acknowledgment: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for grants in support of this work.

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