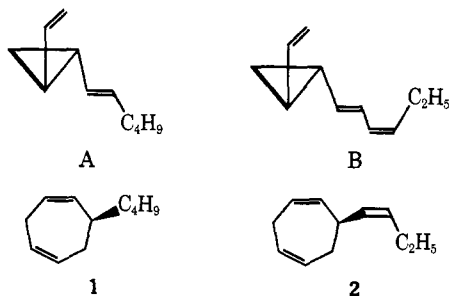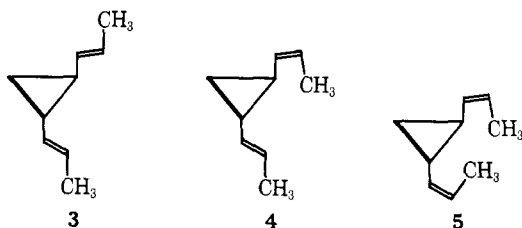the optically active cyclopropanes give optically active cyclohepta-1,4-dienes.


A

B

1

2

To gain information regarding the stereochemical disposition at both migration termini we have prepared and isomerized the three isomeric *trans*-1,2-di(prop-1'-enyl)cyclopropanes **3, 4,** and **5.**

3

4

5

The ttt isomer **3** was prepared from hexa-*trans*-2,-*trans*-4-dienal, through LiAlH$_4$ reduction, Simmons–Smith cyclopropanation,[16] oxidation of the cyclopropylcarbinol with activated MnO$_2$, and coupling of the resultant aldehyde with ethylidenetriphenylphosphorane.[8,17] The hydrocarbon product, purified by glpc on a squalene column, had a strong infrared band at 958 cm^{-1} and the expected mass and nmr spectral characteristics.

The other isomers were obtained from *trans*-cyclopropanedicarboxylate[18] which through LiAlH$_4$ reduction, Ce^{IV} oxidation,[19] and a Wittig condensation led to a mixture of **4** (995 and 712 cm^{-1}) and **5** (713 cm^{-1}).

Isomer **3** is completely converted to *cis*-6,7-dimethylcyclohepta-1,4-diene (**6**) within 4.3 hr at 178°. The nmr spectrum of the C$_9$H$_{14}$ product showed an AB pattern (δ_A 3.07, δ_B 2.55, J_{AB} = 19 Hz) for the nonequivalent protons at C-3.

6

7

8
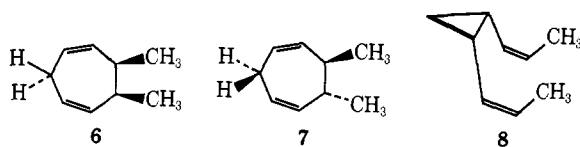
The ttc isomer gave complete conversion to *trans*-6,7-dimethylcyclohepta-1,4-diene (**7**) within 4.2 hr at 179°; the nmr spectrum of the product showed magnetically equivalent C-3 protons at δ 2.79.

Under the same conditions, isomer **5** was partially converted to an equilibrium proportion of *cis,cis,cis*-di-(prop-1'-enyl)cyclopropane (**8**); only a few per cent of the monocyclic product was detected. The structural assignment for the newly produced C$_9$H$_{14}$ material followed from its mass and nmr spectra; the latter showed

an A$_2$BC pattern of cyclopropyl hydrogen absorptions and two equivalent cis double bonds (J_{vic} = 10 Hz).

That the ccc isomer **8** does not rearrange readily at 179° to form dimethylcyclohepta-1,4-diene must be associated with severe methyl–methyl repulsions in conformation **9**; similar stability with respect to Cope rearrangement has been observed in 3,3-dimethyl-*cis*-1,2-dialkenylcyclopropanes.[20,21]

9
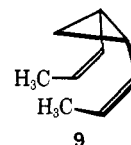
The highly stereoselective and stereospecific reactions shown by the isomeric 1,2-di(prop-1'-enyl)cyclopropanes are consistent with a mechanistic sequence involving first epimerization, then, for the tct and tcc isomers, a normal Cope rearrangement through a boat-like geometry at the transition state. An alternative hypothesis, direct formation of cycloheptadienes through diradical intermediates, fails to account as plausibly for the observed differences among the three *trans*-dipropenylcyclopropanes: if it were the mechanism, all three substrates would be expected to give Cope products at comparable rates. The epimerization process itself might involve diradical intermediates, or conceivably a thermally allowed[22] Smith inversion.[23] Further work on the epimerization mechanism is in progress.

(20) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

(21) T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, **37**, 466 (1972).

(22) R. Hoffmann, R. W. Alder, and C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **92**, 4992 (1970).

(23) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

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Formation of 2-Indanone and Benzocyclobutene from the Pyrolysis of Phenyl Propargyl Ether[1]

Sir:

We have found that the low-pressure (10^{-3}–10^{-5} Torr) gas-phase pyrolysis[2] of phenyl propargyl ether[4–6] gives rise to fair yields of 2-indanone and benzocyclo-

(16) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(17) M. Schlosser and K. F. Christmann, *Justus Liebigs Ann. Chem.*, **708**, 1 (1967).

(18) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

(19) L. B. Young and W. S. Trahanovsky, *ibid.*, **32**, 2349 (1967).

(1) (a) Based on work by P. W. M. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University. (b) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work by Grant No. 3219-A.

(2) The pyrolysis apparatus has been previously described.[3]

(3) W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.* **36**, 3575 (1971).

(4) These ethers were prepared from the appropriate phenol, propargyl chloride or bromide, and potassium carbonate using the method previously described.[5,6]

(5) C. D. Hurd and F. L. Cohen, *J. Amer. Chem. Soc.*, **53**, 1068 (1931).

(6) Y. Okajima, *Yakugaku Zasshi*, **80**, 318 (1960); *Chem. Abstr.*, **54**, 18487h (1960).

butene. The products were identified by their nmr and ir spectral data.

14% recovered   26%   31%
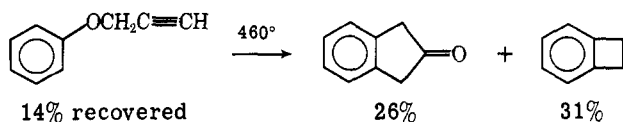
Pyrolyses of 2,6-dimethylphenyl propargyl ether[4,7] and α,α-dimethylpropargyl phenyl ether[4,9] gave rise to fair yields of 2-indanones but no benzocyclobutenes. The yields and structures of the products from pyrolyses at various temperatures are reported in Table I. The structures of the two new dimethylindanones were determined by the data given in the footnotes of Table I.

Table I. Products and Their Yields from the Pyrolysis of Phenyl Propargyl Ethers

Ether	Pyrolysis temp, °C	Product(s) yield, %[a]		Recovered starting material,[a] %
PhOCH₂C≡CH		[b]	[c]	
	460	31	26	14
	440	31	25	18
	400	6	4	90
2,6-(CH₃)₂C₆H₃O-CH₂C≡CH		[d]		
	410	65		Trace
	480	51		
PhOC(CH₃)₂C≡CH		[e]		
	400	61		Trace
	400	57		Trace

[a] Yields determined by nmr spectroscopy using an internal standard, diphenylmethane or tert-butyl bromide. [b] Consistent with published data: G. Fraenkel, Y. Asahi, M. S. Mitchell, and M. P. Cava, Tetrahedron, 20, 1179 (1964). [c] Consistent with published data: E. J. Moriconi, J. P. St. George, and W. F. Forbes, Can. J. Chem., 44, 759 (1966). [d] Nmr (CCl₄) δ 7.71 (br s, 3), 3.32 (q, J = 7 Hz, 1), 3.25 (s, 2), 2.20 (s 3), and 1.33 (d, J = 7 Hz, 3); ir (neat) 1760 cm⁻¹. Anal[8] of 2,4-dinitrophenylhydrazone (mp 202–203°). Calcd for C₁₆H₁₆N₄O₄: C, 60.00; H, 4.71; N, 16.50. Found: C, 59.99; H, 5.04; N, 16.55. [e] Nmr (CCl₄) δ 7.07 (s, 4), 3.33 (s, 2), and 1.20 (s, 6); ir (neat) 1757 cm⁻¹. Anal[8] of 2,4-dinitrophenylhydrazone (mp 190–191°). Calcd for C₁₇H₁₆N₄O₄: C, 60.00; H, 4.71; N, 16.50. Found: C, 59.99; H, 4.73; N, 16.63.

The liquid phase rearrangements of phenyl propargyl ethers have been studied by Schmid and coworkers.[10,11]

(7) Bp 110° (15 mm); nmr (CCl₄) δ 6.82 (br s, 3), 4.33 (d, J = 2.5 Hz, 2), 2.29 (t, J = 2.5 Hz, 1), and 2.23 (s, 6). Anal[8] Calcd for C₁₁H₁₂O: C, 82.47; H, 7.54. Found: C, 82.13; H, 7.48.
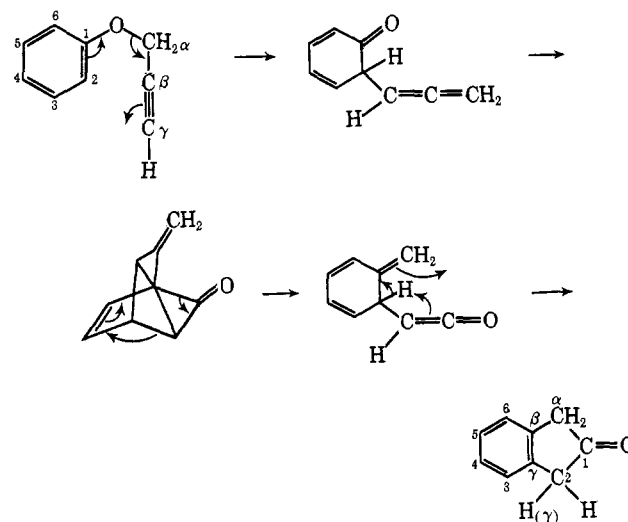(8) Chemalytics, Inc., Tempe, Ariz.
(9) Bp 35° (10⁻³ mm); nmr (CCl₄) δ 7.3–6.7 (m, 5), 2.39 (s, 1), and 1.59 (s, 6); the instability of this ether prevented us from obtaining a sample which gave an acceptable elemental analysis. α,α,γ-Trimethylpropargyl phenyl ether was also so unstable that it could not be purified well enough to give an acceptable elemental analysis.[5]
(10) J. Zsindely and H. Schmid, Helv. Chim. Acta, 51, 1510 (1968).
(11) H. J. Hansen and H. Schmid, Chimia, 24, 89 (1970).

They proposed that the first step of the reaction was a Claisen-type rearrangement to give an allene. If there were no ortho hydrogen atoms on the phenyl group, the allene underwent an intramolecular Diels–Alder reaction giving a tricyclic ketone as product. In fact, they report that these tricyclic ketones can be converted to 2-indanones but no details are given.[11] If ortho hydrogen atoms were present, the allene underwent an enolization reaction giving a different type of product.

Based on Schmid's work, we propose the following mechanism for the formation of the 2-indanones in the gas phase. This mechanism involves four thermally allowed six-electron concerted reactions.[12] The posi-

tions of the methyl groups of both dimethyl-2-indanones are consistent with this mechanism. The mechanism predicts that 2,6-dimethylphenyl propargyl ether should give rise to indanone 1 and indeed the nmr

1
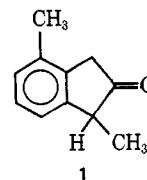
data of the product indicate that one of the methyl groups is on the aromatic ring, but do not indicate an exact position for this methyl group.

2

3

D = 100% deuterium
* = 19% deuterium
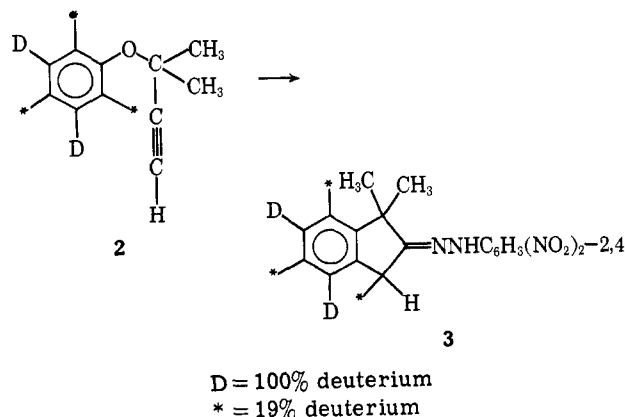
(12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Academic Press, Inc., Weinheim, Germany, 1971.

In order to further test our proposed mechanism, the deuterated phenyl propargyl ether **2** was prepared and pyrolyzed. The deuterium distribution of the phenyl used to prepare **2** was determined to be 19% in the ortho and para positions and *ca.* 100% in the meta positions.[13] The 2,4-dinitrophenylhydrazone of the 1,-1-dimethyl-2-indanone obtained from the pyrolysis of **2** was prepared, and its deuterium distribution as determined by nmr analysis is that shown in **3**. This deuterium distribution is the one predicted by the above mechanism.

The production of the benzocyclobutene from the pyrolysis of the unsubstituted phenyl propargyl ether does not come from the decarbonylation of 2-indanone. A sample of 2-indanone was submitted to our pyrolysis conditions and recovered almost quantitatively.

(13) The deuterated phenol was prepared by converting benzene-d_6 to aniline[14] which was then diazotized and hydrolyzed to phenol.[15] The nmr spectrum of this product indicated that the ortho and para deuterium atoms had been exchanged for hydrogen atoms during its preparation. The nmr signals of the ortho and para protons of phenol are *ca.* 0.5 ppm upfield and those of the meta protons are *ca.* 0.2 ppm upfield from that of benzene.[16] The phenol was converted to anisole and analysis of it by nmr and mass spectroscopy indicated that the meta positions were fully deuterated and the ortho and para position contained 19 % deuterium.

(14) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955.

(15) H. E. Ungnade and E. F. Orwoll, "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 130.

(16) J. C. Schug and J. C. Deck, *J. Chem. Phys.*, 37, 2618 (1962).

(17) Alfred P. Sloan Research Fellow, 1970–1972.

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A New Simple Method for Rapid, Selective Aromatic Deuteration Using Organoaluminum Dihalide Catalysts

Sir:

The most useful general methods for deuteration of aromatic and aliphatic compounds involve exchange with heavy water in the presence of a homogeneous[1,2] or heterogeneous[3] metal catalyst. Of these catalysts those containing platinum are most satisfactory.[4] With homogeneous $PtCl_4{}^{2-}$, aromatic deuteration is sterically retarded at hindered positions,[3] while with a heterogeneous platinum catalyst similar steric hindrance is encountered[4] as well as coupling of the aromatic as a side reaction.[5] For some aromatic compounds, such as naphthalene, the heterogeneous catalyst requires up to several weeks at 150° for the attainment of equilibrium.

We now report that organoaluminum dihalides, such as ethylaluminum dichloride, catalyze very rapid exchange of hydrogen atoms between aromatic nuclei. Equilibrium is attained within minutes at room temperature and there appears to be no steric hindrance. These catalysts afford a new, very rapid, and simple procedure whereby an aromatic compound can be

(1) J. L. Garnett and R. S. Kenyon, *Chem. Commun.*, 1227 (1971), and references cited therein.

(2) R. J. Hodges, D. E. Webster, and P. B. Wells, *ibid.*, 462 (1971).

(3) J. L. Garnett, *Catal. Rev.*, 5, 229 (1971).

(4) J. L. Garnett, *Proc. Int. Conf. Methods Prep. Stor. Label. Compounds, 2nd*, 689 (1968).

(5) G. E. Calf and J. L. Garnett, *Chem. Commun.*, 373 (1969).

deuterated using as the deuterium source an already deuterated aromatic compound such as perdeuteriobenzene.

In a typical experiment ethylaluminum dichloride (0.01 g) was added by syringe to a mixture of perdeuteriobenzene (0.2 ml) and bromobenzene (0.2 ml) in a small serum-capped vial at room temperature. The reactants were not dried prior to use as traces of water serve as a cocatalyst, greatly enhancing the rate of exchange. Reaction was terminated after a few minutes by the addition of excess water. Analysis of the quantitatively recovered bromobenzene by mass and nmr spectrometry showed that exchange equilibrium had been reached at *all* five aromatic positions. In contrast conventional homogeneous and heterogeneous platinum catalysis leads to exchange in only three positions in bromobenzene and a prolonged time at an elevated temperature is required.[3,4]

A wide range of compounds have been deuterated using the present technique. Examples are given in Table I.

Table I. Compounds Deuterated by Exchange with Perdeuterated Benzene Using $EtAlCl_2{}^a$

Organic substrate	% approach to equilibrium	No. of exchangeable H per molecule
Chlorobenzene	100	5
Bromobenzene	100	5
Ethylbenzene	100	5
tert-Butylbenzene	100	5
p-Xylene	100	4
Mesitylene	100	3
Allylbenzene	100	5
Diphenyl	100	10
Dibenzyl	100	10
p-Terphenyl	100	14
Naphthalene	100	8
Anthracene[b]	0	
Chrysene[b]	0	
Pyrene[b]	0	

a Reaction conditions: room temperature, 30 min. *b* Anthracene, chrysene, and pyrene showed complete exchange of 10, 12, and 10 hydrogen atoms, respectively, after 1 week at 90°.

For some of the condensed polycyclic aromatic hydrocarbons, elevated temperature (90°) is necessary. The relatively low reactivity of pyrene and anthracene may be significant, since these hydrocarbons should be particularly reactive if isotope exchange were a simple electrophilic proton substitution.

Alkanes and alkenes, as well as oxygen- and nitrogen-containing compounds, do not exchange. Thus no deuteration was observed with hexane and cyclopentane. Pyridine and many aromatic compounds substituted by electronegative groups (*e.g.*, anisole, benzaldehyde, benzoic acid, phenol, and aniline) not only fail to exchange but also inhibit the deuteration of other aromatic compounds, presumably because of preferential complex formation with the aluminum catalyst.

Mechanistically, it is plausible to suggest that the catalyst acts as a proton-transfer agent and two aromatic compounds undergo exchange in turn, possibly complexing with the metal atoms of the catalyst through a π-associative-type species as proposed for other catalytic exchange systems.[3,4] A brief, critical, mecha-