CHEMISTRY LETTERS, pp. 359-362, 1974. Published by the Chemical Society of Japan

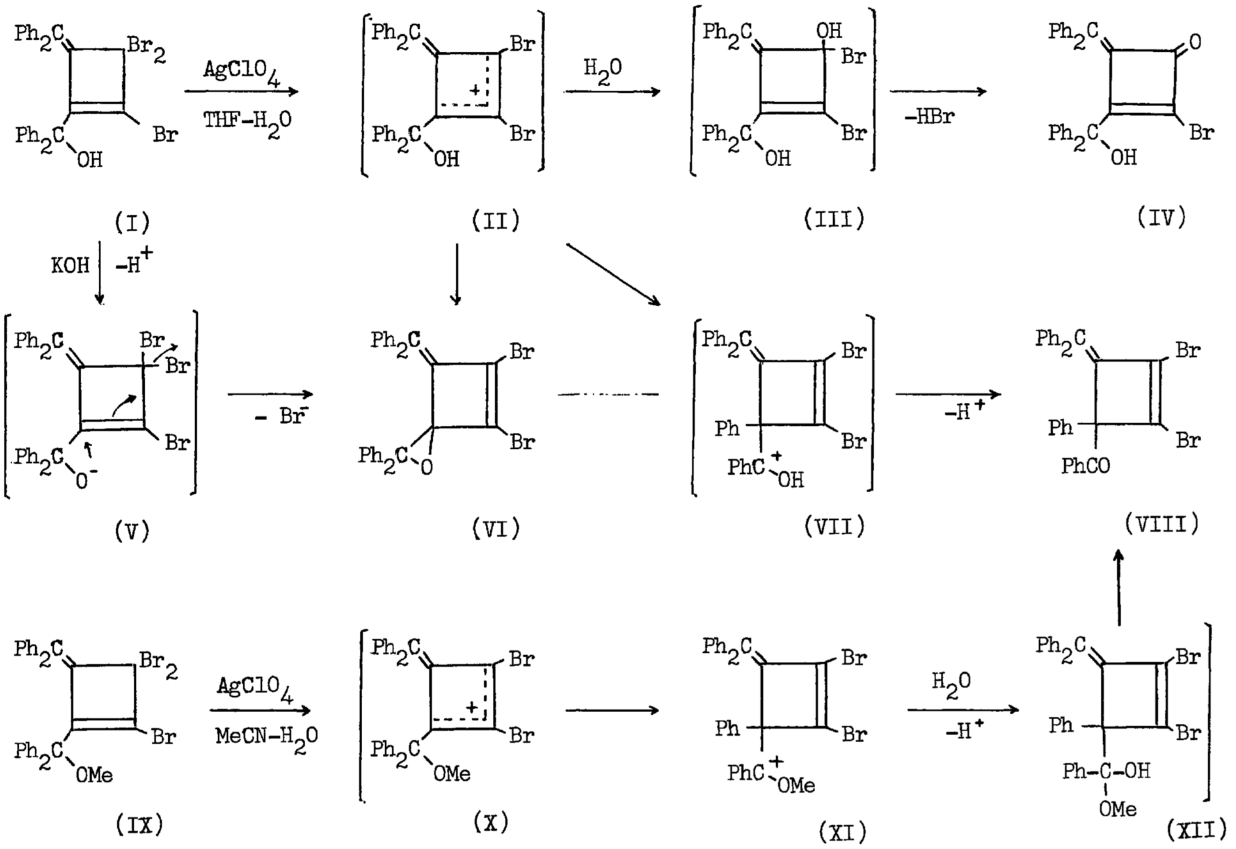
THE SYNTHESIS OF 3-BENZOYL-4-METHYLENECYCLOBUT-1-ENE AND 6-METHYLENE-1-OXASPIRO[2,3]HEX-4-ENE, AND THEIR RING EXPANSION INTO METHYLENECYCLOPENTENONES

Kozaburo UEDA and Fumio TODA
Department of Industrial Chemistry, Faculty of Engineering, Ehime University,
Matsuyama 790

The reaction of 2,3,3-tribromo-1-diphenylhydroxymethyl-4-diphenylmethylenecyclobut-1-ene (I) with $AgClO_4$ afforded new 4,5-dibromo-2,2-diphenyl-6-diphenylmethylene-1-oxaspiro[2,3]hex-4-ene (VI) and 3-benzoyl-1,2-dibromo-3-phenyl-4-diphenylmethylenecyclobut-1-ene (VIII), probably via the methylenecyclobutenylium ion (II). New acid-catalyzed ring expansion reaction of VI to afford 3,4-dibromo-2,2-diphenyl-5-diphenylmethylenecyclopent-3-en-1-one (XIV) and 2,3-dibromo-5,5-diphenyl-4-diphenylmethylenecyclopent-2-en-1-one (XV) was found.

The formation of some cyclobutenylium ions has been reported.[1] However, no methylenecyclobutenylium ion has yet been reported. In order to examine the formation of the methylenecyclobutenylium ions, II and X, we have studied the reactions of 2,3,3-tribromo-1-diphenylhydroxymethyl-4-diphenylmethylenecyclobut-1-ene (I)[2] and its methyl ether (IX) with $AgClO_4$.

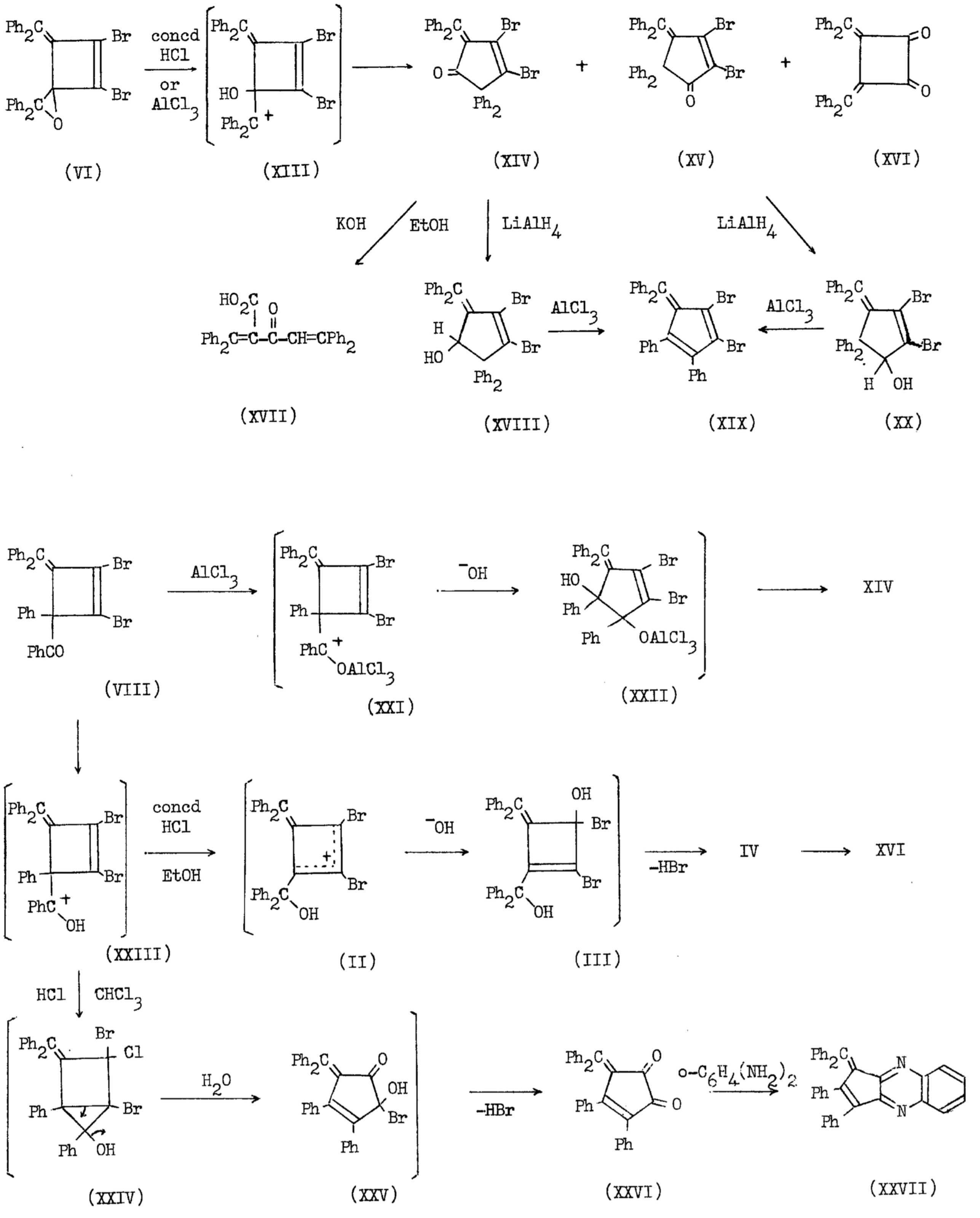
The reaction of I with $AgClO_4$ in H_2O-THF at 80°C afforded 4,5-dibromo-2,2-diphenyl-6-diphenylmethylene-1-oxaspiro[2,3]hex-4-ene (VI, 10%; mp 182.0-183.0°C),[3] 3-benzoyl-1,2-dibromo-3-phenyl-4-diphenylmethylenecyclobut-1-ene (VIII, 37%; mp 126.0-128.0°C), and IV[2] (30%). The reaction can be explained by assuming the methylenecyclobutenylium ion (II) as an intermediate. The ketonizations of III initially produced by the hydroxylation of II, and of VII initially produced by the 1,2-phenyl migration of II afford IV and VIII respectively. The direct cyclization of II affords VI. VI was also obtained by the reaction of I with KOH-MeOH in a quantitative yield. This can be interpreted by means of an intramolecular S_N2' reaction of the anion (V) initially formed by the deprotonation of I. The reaction of IX with $AgClO_4$ in H_2O-MeCN afforded VIII in a 70% yield. This reaction can also be explained by assuming the methylenecyclobutenylium ion (X) as an intermediate, i.e., the ketonization of XII which was produced by the hydroxylation of XI initially formed by the 1,2-phenyl migration of X affords VIII (Scheme 1).



Scheme 1

During the course of the structural studies of VI and VIII, some new ring expansion reactions of them were found. The treatment of VI with $AlCl_3$ in benzene afforded 3,4-dibromo-2,2-diphenyl-5-diphenylmethylenecyclopent-3-en-1-one (XIV, 73%; mp 177.5-178.0°C) and 2,3-dibromo-5,5-diphenyl-4-diphenylmethylenecyclopent-2-en-1-one (XV, 21%; mp 234.0-235.5°C), probably by the ring expansion of the intermediate carbonium ion (XIII). The heating of VI and concd HCl in EtOH also afforded XIV (85%) and XV (10%), and a small amount of XVI$^{4)}$ (2%). The five-membered ring natures of XIV and XV were confirmed by converting them into 2,3-dibromo-4,5,6,6-tetraphenylfulvene (XIX; mp 189.0-189.5°C (lit$^{5)}$ 189.5°C)). The $LiAlH_4$ reductions of XIV and XV afforded the corresponding alcohols, XVIII and XX, respectively. The treatments of XVIII and XX with $AlCl_3$ afforded XIX, probably by dehydroxylation followed by 1,2-phenyl migration and deprotonation. Further structural evidence for XIV was obtained by its reaction with KOH-MeOH to afford XVII (55%; mp 181.0-182.0°C (lit$^{6)}$ 182°C)).

When the $AlCl_3$-catalyzed reaction of VIII was carried out in benzene at 50°C, XIV was also obtained in a quantitative yield. The pathway of the formation of XIV in the reaction of VIII with $AlCl_3$ can be interpreted as follows: The ring expansion of XXI initially formed by coordination of $AlCl_3$ to VIII affords XXII. The subsequent ketonization accompanied by the 1,2-phenyl migration of


(VI)
concd HCl or AlCl$_3$
(XIII)
(XIV)
(XV)
(XVI)
KOH EtOH
LiAlH$_4$
LiAlH$_4$
(XVII)
(XVIII)
AlCl$_3$
(XIX)
AlCl$_3$
(XX)
(VIII)
AlCl$_3$
(XXI)
$^-$OH
(XXII)
XIV
(XXIII)
concd HCl EtOH
(II)
$^-$OH
(III)
-HBr
IV
XVI
HCl CHCl$_3$
(XXIV)
H$_2$O
(XXV)
-HBr
(XXVI)
o-C$_6$H$_4$(NH$_2$)$_2$
(XXVII)

Scheme 2

XXII affords XIV (Scheme 2). In the contrast to the reaction of VIII with $AlCl_3$, the reaction of VIII with concd HCl-EtOH afforded XVI quantitatively. Furthermore, the reaction of VIII with HCl-saturated $CHCl_3$ afforded 3,4-diphenyl-5-diphenylmethylenecyclopent-3-ene-1,2-dione (XXVI, 60%; mp 222.0-223.0°C). The structure of XXVI was identified by the reaction with o-phenylenediamine to afford the quinoxaline derivative (XXVII; mp 247.0-248.0°C). Although reason for the difference between the latter two reactions is not clear, both the reactions can be interpreted by assuming the intermediate carbonium ion (XXIII) initially produced by the protonation to VIII. The 1,2-phenyl migration of XXIII affords II, which converts into IV via III as was shown in Scheme 1. The acid-catalyzed reaction of IV to afford XVI has been established. When the π-electrons of the endo-double bond of XXIII attack the positively-charged benzyl carbon, the bicyclic intermediate (XXIV) is formed. The ketonization of XXV which was derived from XXIV affords XXVI.

The UV spectral data of all new compounds are sumarized in Table 1.

Table 1. The UV Spectral Data of the Reaction Products

Compounds	$\lambda_{max}^{CHCl_3}$ nm ($\varepsilon \times 10^{-2}$)	Compounds	$\lambda_{max}^{CHCl_3}$ nm ($\varepsilon \times 10^{-2}$)
VI	245 sh (147), 303 (193)	XVIII[a)]	208(374), 238 (166), 304 (214)
VIII	255 sh (210), 286 (155)	XXVI	252 sh (160), 354 (247)
XIV	255 sh (147), 354 (146)	XXVII	255 sh (301), 305 (266), 350 (297)
XV	248 sh (152), 275 (111), 352 (133)		

a) Measured in EtOH.

References

1) H. H. Freedman and A. E. Young, J. Amer. Chem. Soc., 86, 734 (1964); R. F. Bryan, ibid., 86, 733 (1964).

2) F. Toda and K. Akagi, Tetrahedron Lett., 1970, 5289.

3) Satisfactory analytical data were obtained for all the new compounds.

4) F. Toda and K. Akagi, Tetrahedron, 27, 2801 (1971).

5) The reaction of 3,4-dibromo-1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene with Br_2 in $CHCl_3$ afforded XIX in a 90% yield; $\lambda_{max}^{CHCl_3}$ 248 (21700) and 380 nm (ε, 22700); F. Toda and M. Sasaoka, unpublished data.

6) G. A. Taylor, Chem. Commun., 1314 (1968).

(Received February 6, 1974)