

CYCLOBUTANE RING OPENING OF ALLENE-ENONE
PHOTOADDUCTS BY MERCURY (II) PERCHLORATE

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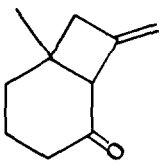
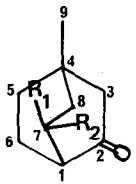
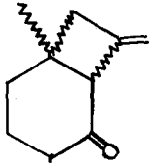
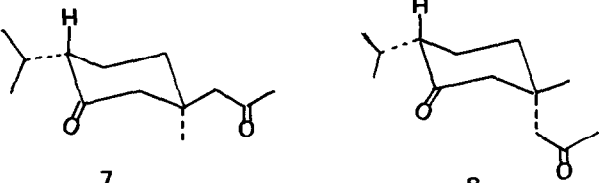
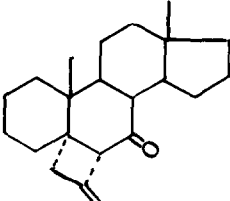
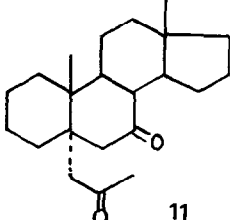
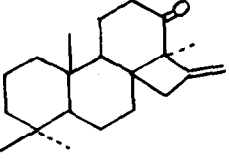
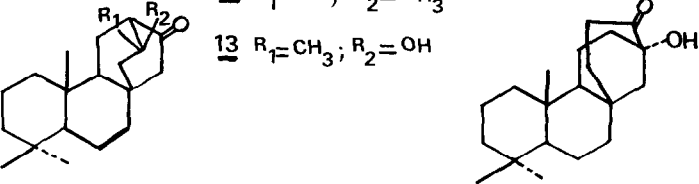
Abstract : Cyclobutane ring opening of some allene-enone photoadducts by $\text{Hg}(\text{ClO}_4)_2$ in acetone gave diketones which led, in some cases, to bicyclic ketols through intramolecular aldol condensation .

In previous communications, we have reported the acid-catalysed rearrangement with *p*-toluenesulfonic acid¹ and the cyclobutane ring opening by boron trifluoride² of some allene-enone photoadducts (1 to 4) . The structures of these reactions products suggested that they are formed through the initial attack of the electrophile (H^+ or $\text{BF}_3\text{-Et}_2\text{O}$) at the carbonyl group . On the other hand, soft electrophiles, like mercury (II) salts, prefer to bind to alkenes³ and mercuration-demercuration reactions of olefins are well documented⁴ . In this paper, we wish to describe the behaviour of compounds 1 to 4 in presence of mercury (II) perchlorate⁵ (Table) .

Reactions were carried out in acetone under the following typical conditions : A solution of 3 (300 mg) in acetone (3 ml) was added to a stirred solution of $\text{Hg}(\text{ClO}_4)_2$ (1,5 molar equivalent) in acetone (3 ml) . The reaction was monitored by t.l.c. and disappearance of the starting material was usually achieved within 30 min. . Evaporation of the solvent and extraction with ether led to the crude product which was purified by chromatography on silica gel to afford the diketone 11 (175 mg) m.p. (ether) 134-135°C ; $\nu(\text{CCl}_4)$ 1710-1720 cm^{-1} , $\delta(\text{CDCl}_3)$ 0.70 (s, 3H), 1.27 (s, 3H), 2.13 (s, 3H) ; ^{13}C n.m.r. δ 212 and 207 (2s, >C=O) ; m.s. M^+ 300 and m/z 43 .

Similar treatment of 2 gave diketones 7 and 8 in 75 % yield . They revealed the same m.s. (M^+ 210 and m/z 43) and i.r. (ν 1710-1720 cm^{-1}) but different ^1H n.m.r., ^{13}C n.m.r.

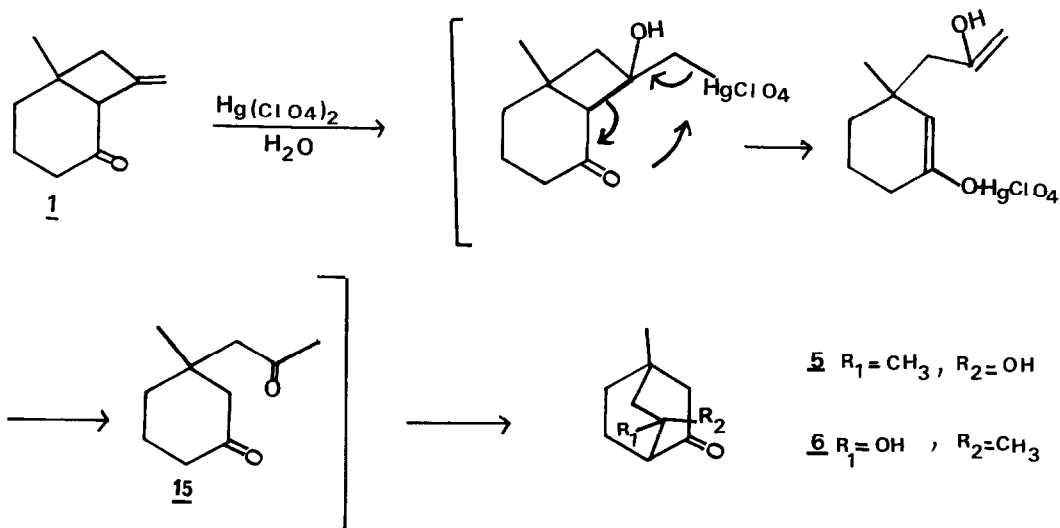
T A B L E

Photoadducts	Products
 <p style="text-align: center;"><u>1</u></p>	 <p style="text-align: center;"><u>5</u> $R_1 = \text{CH}_3$; $R_2 = \text{OH}$ <u>6</u> $R_1 = \text{OH}$; $R_2 = \text{CH}_3$</p>
 <p style="text-align: center;"><u>2</u></p>	 <p style="text-align: center;"><u>7</u> <u>8</u></p>
 <p style="text-align: center;"><u>3</u></p>	 <p style="text-align: center;"><u>11</u></p>
 <p style="text-align: center;"><u>4</u></p>	 <p style="text-align: center;"><u>12</u> $R_1 = \text{OH}$; $R_2 = \text{CH}_3$ <u>13</u> $R_1 = \text{CH}_3$; $R_2 = \text{OH}$</p> <p style="text-align: right;"><u>14</u></p>

spectra and Rf. . 7 (the more polar Rf = 0.3 - 0.4), δ 0.88 (d, J = 6 Hz, 6H), 0.98 (s, 3H), 2.13 (s, 3H) . 8 (the less polar, Rf = 0.4 - 0.5), δ 0.88 (d, J = 6 Hz, 6H), 1.10 (s, 3H), 2.11 (s, 3H)⁶ .

While compounds 2 and 3 gave stable diketones (11 and 7, 8 respectively), compound 1 afforded, under the same conditions, bicyclic ketols 5 and 6 in 60 % yield . Pure 5 was separated by recrystallization from ether-pentane : m.p. 130-131°C, $\nu(\text{CH}_2\text{Cl}_2)$ 3535, 1720 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.00 (s, 3H), 1.39 (s, 3H), 1.98 (d, 1H, J = 19 Hz, H₃ endo), 2.22 (d, 1H, J = 19 Hz, H₃ exo) ; ¹³C n.m.r. $\delta(\text{CDCl}_3)$ 20.5 (t, C₆), 26.5 (q, C₉), 28.6 (q, C₁₀), 31.5 (t, C₅), 33.5 (s, C₄), 48.8 (t, C₈), 49.5 (t, C₃), 55.6 (d, C₁), 72.1 (s, C₇), 212 (s, C₂) . In the same way 4 gave three ketols 12, 13 and 14 in 50 % yield⁷ . These products were separated by chromatography on silica gel AcOEt-hexane 1/3 : 12 (41 %) Rf = 0.5 - 0.6 ; m.p. (ether) 154-156.5°C ; $\nu(\text{CCl}_4)$ 3600, 3440, 1730 and 1720 cm^{-1} ; $\delta(\text{CDCl}_3)$ 0.83, 0.86 (2s, 2 CH₃), 1.08 (s, 3H), 1.20 (s, 3H) . 13 (27 %) Rf = 0.3 - 0.4 ; m.p. (ether) 193-195°C ; $\nu(\text{CCl}_4)$ 3580, 3400, 1735 and 1720 cm^{-1} ; $\delta(\text{CDCl}_3)$ 0.83, 0.86 (2s, 2 CH₃), 0.96 (s, 3H), 1.36 (s, 3H) . 14 (32 %) Rf = 0.1-0.2 ; m.p. (ether) 178-179°C ; $\nu(\text{CCl}_4)$ 3600, 1710 cm^{-1} , $\delta(\text{CDCl}_3)$ 0.86 (s, 3H), 1.03 (s, 6H) .

Since the reaction is performed in acetone without any reducing reagent, cyclobutane ring opening of photoadducts 1 to 4 by mercury (II) perchlorate probably proceeds through a neighboring group participation of the carbonyl group⁸ . For instance, compound 1 gave bicyclic ketols 5 and 6 through intramolecular aldol condensation of the intermediate diketone 15 as indicated in the scheme .

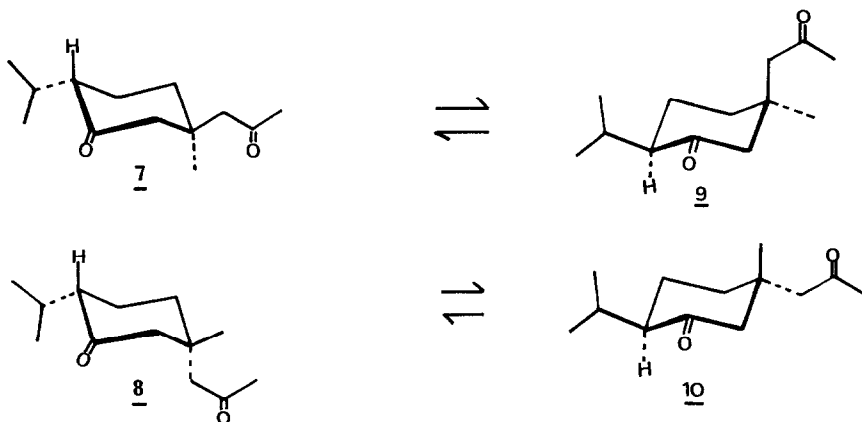


S C H E M E

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R E F E R E N C E S a n d N O T E S

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- 3 . R. G. PEARSON, "Hard and Soft Acids and Bases", Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1973 ; T.L. HO, Chem. Rev., 75, 1 (1975) .
- 4 . H. C. BROWN and P. J. GEOGHEGAN, J. Org. Chem., 35, 1844 (1970) ; R. LAROCK, Angew. Chem. Int. Ed. Engl., 17, 27 (1978) ; D. SEYFERTH, J. Organometallic Chem., 203, 183 (1980) .
- 5 . Commercial mercury (II) perchlorate was purified by recrystallization from water and stored in a vacuum desiccator .
- 6 . It is to be noted that in chloroform solution, the diketone 7 was in equilibrium with its epimer 9, which is the enantiomer of 8 . In the same conditions, the diketone 8 was in equilibrium with 10 which is the enantiomer of 7 .



- 7 . These products were also formed when the ethylene-ketal derivative from 4 was allowed to react with $\text{Hg}(\text{ClO}_4)_2$ in the conditions described above .
- 8 . Such a mechanism has been observed by H. YOSHIOKA, K. TAKASAKI, M. KOBAYASHI and T. MATSUMOTO, Tetrahedron Lett., 3489 (1979) .

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