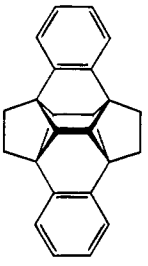
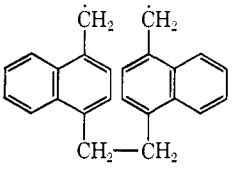
The mass spectrum shows a molecular ion peak at *m/e* 308 and a base peak at *m/e* 154. The ultraviolet spectrum (Figure 1) is strikingly similar to that of 1,4-dimethylnaphthalene and shows the typical bathochromic shifts characteristics of [2.2]cyclophanes.[6] In particular, the band at 244 mμ associated[1] with transannular effects is clearly evident.

The nmr spectrum, shown in Figure 2, provides strong support for the assigned (*syn*) structure. It is particularly interesting to compare this spectrum with the spectra of the *anti* form Ia and of 1,4-dimethylnaphthalene. As expected, the more highly shielded H_a and H_b protons of Ib show upfield absorption (symmetrical A_2B_2 multiplet, 8 H, centered at τ 2.85) compared to the H_a and H_b protons of Ia (m, 8 H, τ 2.5). The latter, in turn, have essentially the same chemical shifts as the corresponding protons of 1,4-dimethylnaphthalene. On the other hand, there is a striking difference between the peaks associated with H_c protons in the *syn* and *anti* forms. In the *anti* isomer, these H_c protons (s, 4 H, τ 4.28) are rigidly held in the fields of the transannular naphthalene nuclei and are shifted significantly upfield, while the H_c *syn* protons (s, 4 H, τ 3.28) experience relatively less shielding. The spectrum of the *syn* compound also contains a symmetrical multiplet at τ 6.42 assigned to the eight ethylene bridge protons.

When Ib is heated above its melting point, it resolidifies at 250° and remelts at 300–303°, the melting point of the *anti* form.[1] The ultraviolet and nmr spectra of the resolidified material confirm the fact that complete conversion to the *anti* isomer takes place in this thermal process. Interconversion of the *syn* and *anti* forms may also be accomplished by photochemical means. Thus, irradiation[7] of pure Ib in degassed benzene at 3500 Å for 10 days yields predominantly (*ca.* 70%) isomer Ia with only traces of *syn* material remaining.[8] On the other hand, nmr analysis of the reaction mixture from photolysis[9] of pure *anti* isomer Ia in benzene clearly shows the presence of minor amounts of *syn* product Ib along with dibenzoequinine IV[10] (25%) and unreacted Ia (70%). Conversion of Ib to Ia most probably takes place through strain-relieving rupture of the ethylene bridge to form V which may then reclose to form the more stable *anti* isomer.



IV



V

(5) The X-ray structure determination by Dr. Albert Fratini, University of Dayton, will be reported separately.

(6) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).

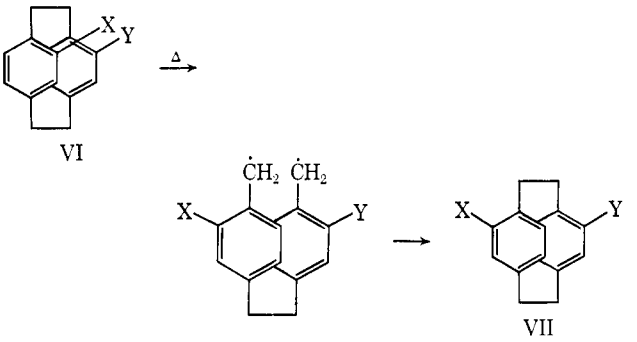
(7) A Rayonet photochemical reactor was the light source.

(8) At the same time about 20% of dibenzoequinine[10] was also formed, presumably from the further photolysis of the *anti* isomer.

(9) As previously reported, the irradiation of Ia in benzene–methanol yields dibenzoequinine but no Ib.

(10) H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **89**, 2270 (1967).

Analogy for the formation of V may be found in the earlier work of Reich and Cram[11] who have demonstrated that thermal cleavage to biradical intermediates occurs in substituted [2.2]paracyclophanes, as in the isomerization of systems VI to VII.



VI VII

Acknowledgments. This work was supported by National Institutes of Health Grant GM 13854. We thank Dr. Walter McMurray for the mass spectrum determination.

(11) H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967).

(12) National Institutes of Health Predoctoral Fellow, 1966–1968.

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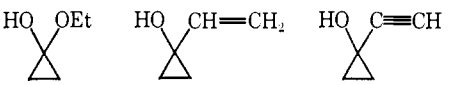
Cyclopropanone Reactions. Cyclobutanone Derivatives from Vinylic and Acetylenic Cyclopropanols

Sir:

We have recently reported[1] that the ethyl hemiketal of cyclopropanone (I) provides a convenient source of the parent ketone for reactions with nucleophilic reagents. We now wish to describe examples of such reactions with vinylic and acetylenic Grignard reagents leading to novel cyclopropanol derivatives which may serve as convenient precursors of substituted cyclobutanones.



I II III

Addition of I[2,3] to an excess of vinylmagnesium bromide in refluxing THF yielded 1-vinylcyclopropanol (II; 64%): bp 44–51° (28 mm); nmr (CCl_4) τ 4.15–5.15 (m, 3 H), 5.55 (s, 1 H), and 9.21 (m, A_2B_2, 4 H); ir (liquid film) 3340, 3100, 3020, and 1645 cm^{-1}; mol wt (mass spectrum), 84; acetyl derivative:[4] nmr τ 4.05–4.50 (m, 1 H), 4.95–5.30 (m, 2 H), 8.08 (s, 3 H),

(1) H. H. Wasserman and D. C. Clagett, *J. Amer. Chem. Soc.*, **88**, 5368 (1966).

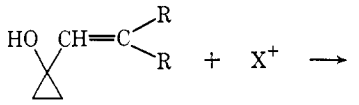
(2) The ethyl hemiketal may be conveniently prepared (43%) by the reaction of diazomethane with excess ketene in ether at −78°, in the presence of ethanol. Unreacted ketene is removed by extraction with aqueous bicarbonate solution. I, bp 60–62° (20 mm), may be purified by distillation and stored at 0° for several weeks without decomposition.

(3) In this work no attempt was made to generate solutions of the free ketone at low temperature as described by N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3672 (1966). See also S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim.*, **85**, 1170 (1966).

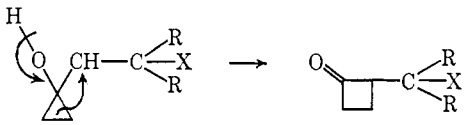
(4) The acetate was formed by treatment of II with 1 equiv of ethylmagnesium bromide followed by acetyl chloride.

and 9.08 (m, 4 H). *Anal.* Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.41; H, 8.00.

Compound II undergoes ready ring expansion with a variety of electrophilic reagents to form cyclobutanones. The rearrangement takes place most probably through the intermediate cyclopropylcarbinyl cation.[5]



IV



a, X = H
b, X = Cl
c, X = OH
d, X = $CH_2N(R')_2$

V

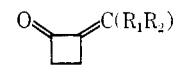
Thus, excess HBr in methylene chloride converted II to 2-methylcyclobutanone[6-8] (V, R = X = H; 83%): ir (CCl_4) 1785 cm^{-1}; nmr (CCl_4) τ 6.50–8.70 (m, 5 H), 8.85 (d, 3 H). With perbenzoic acid in ether, II yielded 2-hydroxymethylcyclobutanone (V, R = H; X = OH): bp 100–105° (5 mm) (32%); ir (CCl_4) 3480 and 1780 cm^{-1}; nmr (CCl_4) τ 5.90–6.80 (m, 4 H), 6.85–7.25 (m, 2 H), and 7.65–8.30 (m, 2 H). 2-Hydroxymethylcyclobutanone was further characterized as its acetate derivative.[6] Likewise, chlorination with *t*-butyl hypochlorite in chloroform gave ring enlargement[9] to form 2-chloromethylcyclobutanone[6] (V, R = H; X = Cl; 81%): bp 75–78° (17 mm); ir (CCl_4) 1790 cm^{-1}; nmr (CCl_4) τ 6.10–6.50 (m, 3 H), 6.70–7.20 (m, 2 H), and 7.50–8.30 (m, 2 H).

With trioxymethylene and a secondary amine hydrochloride in refluxing ethanol, 1-vinylcyclopropanol underwent a novel type of Mannich reaction producing substituted aminoethylcyclobutanones. Using dibenzylamine hydrochloride in this reaction, V (R = H; X = $CH_2N(CH_2Ph)_2$) was obtained (60%): mp 80.5–82°; ir 1780 cm^{-1}; nmr τ 2.80 (s, 10 H), 6.55 (s, 4 H), 6.7–7.6 (m, 5 H), and 8.0–8.6 (m, 4 H); mol wt, 293.1780 (mass spectrum). *Anal.* Calcd for $C_{23}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.95, H, 7.89; N, 4.77.

Starting from the substituted 1-vinylcyclopropanol (IV, R = CH_3),[10] reaction with *t*-butyl hypochlorite at 0° in chloroform and with *m*-chloroperbenzoic acid in chloroform led to V (R = CH_3; X = Cl;[6] 80%; and R = CH_3; X = OH;[6] 65%, respectively). With proton donors, however, opening of the cyclopropane ring was the predominant reaction producing the unsaturated ketone VII and products resulting from addition to this species.

$CH_3CH_2COCH{=}C(CH_3)_2$
VII

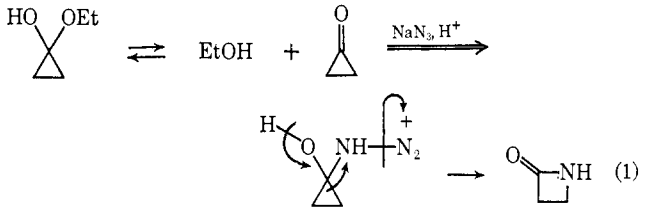
The addition of I to a refluxing solution of ethynylmagnesium bromide in THF yielded III (21%): bp 45–50° (20 mm); ir (CCl_4) 3580, 3350, 3300, and 3090 cm^{-1}; nmr (CCl_4) τ 5.90 (s, 1 H), 7.62 (s, 1 H), and 9.00 (m, 4 H); acetyl derivative: nmr (CCl_4) τ 7.61 (s, 1 H), 7.98 (s, 3 H), and 8.85 (m, 4 H). *Anal.* Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.55; H, 6.54. The acetylenic alcohol was surprisingly unreactive toward aqueous HCl or *m*-chloroperbenzoic acid. However, with *t*-butyl hypochlorite it was transformed (60%) to 2-chloromethylenecyclobutanone (VIIIa): mp 25°; ir (CCl_4) 1765 and 1640 cm^{-1}; nmr (CCl_4) τ 3.10 (m, 1 H) and 6.82–7.50 (m, 4 H); $\lambda_{max}^{CH_3CN}$ 242.5 mμ (ϵ 14,700). *Anal.* Calcd for C_5H_5ClO: C, 51.52; H, 4.32; Cl, 30.41. Found: C, 51.68; H, 4.27; Cl, 30.50



VIIIa, R_1 = H; R_2 = Cl
b, R_1 = R_2 = H
c, R_1 = R_2 = CH_3

Other methylenecyclobutanones were readily obtained during this study by dehydrohalogenation of V (R = H; X = Cl; and R = CH_3; X = Cl) with triethylamine in THF. The products thus obtained were VIIIb[6,11] (50%) and VIIIc[6,12] (70%).

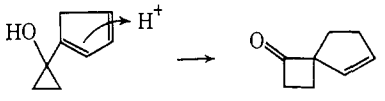
It is of interest to report that a related ring enlargement was observed in the reaction of I (0.04 mol) with sodium azide (0.20 mol) in acetone at pH 5.5 (KH_2PO_4–NaOH buffer) whereby β-lactam[6,13] (21%) was formed: mp 73.5–74.5°; ir ($CHCl_3$) 3430 and 1750 cm^{-1}; nmr ($CDCl_3$) τ 3.20 (broad s, 1 H), 6.60–6.80 (m, 2 H), and 6.90–7.12 (m, 2 H). The rearrangement is given in eq 1.



(1)

Acknowledgments. This work was supported by National Institutes of Health Grant GM 07874.

(5) An earlier example of this type of rearrangement is found in the reaction of the acetate of I with cyclopentadienylmagnesium bromide yielding i which, with acid, rapidly reverts to ii.[1]



i ii

(6) Satisfactory C, H (and N, when present) analyses were obtained by Dr. R. Rittner, Hamden, Conn.

(7) Treating II with perchloric acid in aqueous acetone yielded ethyl vinyl ketone (20%) in addition to the ring-expanded product V (20%).

(8) J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965).

(9) Related ring-expansion reactions by the action of *t*-butyl hypochlorite on higher members of the 1-alkenylcycloalkanol series have been reported by C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).

(10) Formed from the reaction of isobutenylmagnesium bromide with I (65%): bp 65–70° (18 mm); ir (liquid film) 3310, 3080, 1670, and 1620 cm^{-1}; nmr (CCl_4) τ 4.67 (m, 1 H), 6.80 (s, 1 H), 8.20 (d, 3 H), 8.35 (d, 3 H), and 9.35 (m, 4 H). A satisfactory C and H analysis was obtained on the acetyl derivative.

(11) The spectroscopic properties (ir, nmr, and uv) of 2-methylenecyclobutanone (VIIIb) which undergoes rapid polymerization even at −10° are in accord with those reported very recently by von M. Mühlstädt and H. Meinhold, *J. Prakt. Chem.*, 37, 162 (1968).

(12) 2-Isopropylidenecyclobutanone was previously reported by J. M. Conia and J. P. Sandre, *Bull. Soc. Chim. Fr.*, 744 (1963).

(13) R. W. Holley and A. D. Holley, *J. Amer. Chem. Soc.*, 71, 2129 (1949); S. Searles and R. E. Wann, *Chem. Ind.* (London), 2097 (1964); K. D. Barrow and T. M Spotswood, *Tetrahedron Lett.*, 3325 (1965).

(14) National Institutes of Health Predoctoral Fellow, 1965–1969.

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