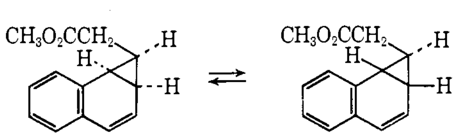
$-80°$ only one ketene (**6d**) is formed, and addition of methanol at $-80°$ gives only the *endo* ester **7**. The



7 8

*endo* ester equilibrates with the *exo* ester at room temperature (*endo*:*exo* 35:65). The activation parameters for the *endo* to *exo* ester isomerization are $\Delta H^{\ddagger} = 22.1$ kcal/mole, $\Delta S^{\ddagger} = -6.5$ eu. The rate constant, $k$, for the isomerization at 25° is $5.10 \times 10^{-6}$ sec$^{-1}$. These values compare favorably with those reported for benzonorcaradiene.[7]

Photoisomerization of **4d** to a labile dihydronaphthalenone at room temperature has been reported.[6] This photoisomerization is a minor competitor with ketene **6d** formation at low temperatures. Experiments at $-190°$ show that the dihydronaphthalene and the ketene **6d** are both primary photoproducts.

In the absence of nucleophiles, the major thermal reactions of the ketenes **6a,b,d** are recyclization to **4a,b,d** and dimerization.

The photoisomerization of bicyclic dienones described above is apparently general and gives high yields of products in a stereospecific manner. It provides an attractive route to novel heterocyclic systems and to all *cis*-cyclopropane derivatives.

**Acknowledgment.** This research was supported by grants from the National Science Foundation (GP-10164), the National Institute of General Medical Sciences (GM-14305), and the Mobil Foundation. The 100-MHz nmr spectrometer was purchased with funds provided by the National Science Foundation (GP-6966).

(7) E. Vogel, D. Wendisch, and W. Roth, *Angew. Chem. Intern. Ed. Engl.*, 3, 443 (1964).

(8) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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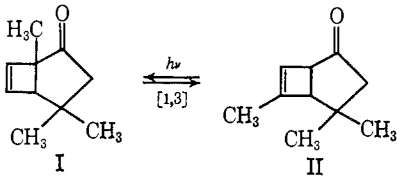
## Competitive [1,3] *vs.* [3,3] Sigmatropic Photorearrangements in Bicyclo[3.2.2]nonatrienones

*Sir:*

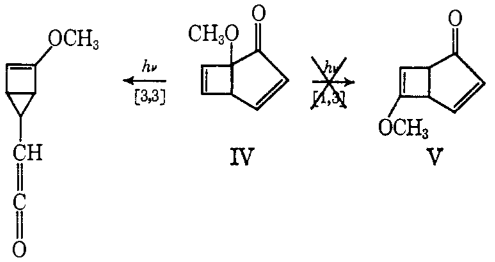
Absorption of light by $\beta,\gamma$-unsaturated ketones leads characteristically to [1,3] sigmatropic[1] shifts exemplified by the photoequilibrium between ketones I and II discovered by Büchi and Burgess.[2] Where the $\beta,\gamma$-enone



I II

system is further extended by $\alpha',\beta'$ unsaturation, as is the case for phototropolone methyl ether (IV), there is observed a different photochemical pathway leading to the ketene III by what is formally a [3,3] sigmatropic rearrangement.[3]

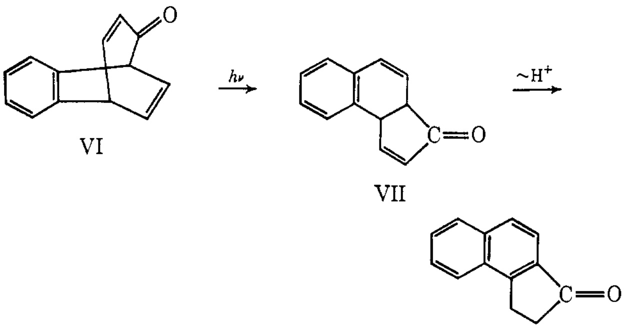
While the ketone IV reportedly shows no propensity for the alternative [1,3] sigmatropic shift to produce V, we now describe a related class of compounds for which both [1,3] and [3,3] photorearrangements may be detected and products derived from either pathway made to predominate depending on reaction conditions.



IV V

III

An earlier communication has noted the facile photoisomerization of the tropone–benzyne adduct VI in acetonitrile to the labile dihydronaphthalene ketone VII which is rapidly and irreversibly converted by weak bases to the prototropic rearrangement product VIII.[4]



VI

VII

VIII

We have recently observed that in aqueous solvents the photochemistry of ketone VI takes a new course to give, besides traces of VII, predominantly an acidic product from which a single crystalline $C_{13}H_{12}O_2$ carboxylic acid,[5] mp 92–93°, may be obtained by careful manipulations. The ultraviolet spectrum of this photoacid closely resembles that of the benzonorcaradiene acid IXa,[6] and the nmr spectrum also parallels that of IXa except for an additional two-proton doublet ($J$ = 7 Hz) at $\delta$ 2.53. Together with the mass spectrum[7] (major peaks at $m/e$ 200, 155, 141, 128) these data point to the structure Xa for the photoacid, and this assignment has been confirmed by its synthesis in good yield from the acid IXa through the crystalline diazo ketone IXb, mp 108–110°, using a photochemical Wolff rearrangement.[8]

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(1) For nomenclature and notation, see R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

(2) G. Büchi and E. M. Burgess, *ibid.*, 82, 4333 (1960).

(3) O. L. Chapman and J. D. Lassila, *ibid.*, 90, 2449 (1968).

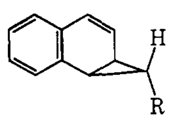
(4) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, 89, 2778 (1967).

(5) All new compounds have been characterized by ir, nmr, and satisfactory analytical data.

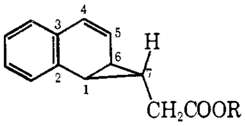
(6) R. Huisgen and G. Juppe, *Chem. Ber.*, 94, 2332 (1961).

(7) Mass spectra were taken on a Perkin-Elmer-Hitachi RMU6E instrument; we are indebted to the National Science Foundation for a grant toward purchase of this spectrometer.

(8) L. Horner, E. Spietschka, and A. Gross, *Ann.*, 573, 17 (1951). Acid Xa could also be obtained in poor yield through a conventional silver oxide catalyzed decomposition of diazo ketone IXb in methanol followed by hydrolysis.

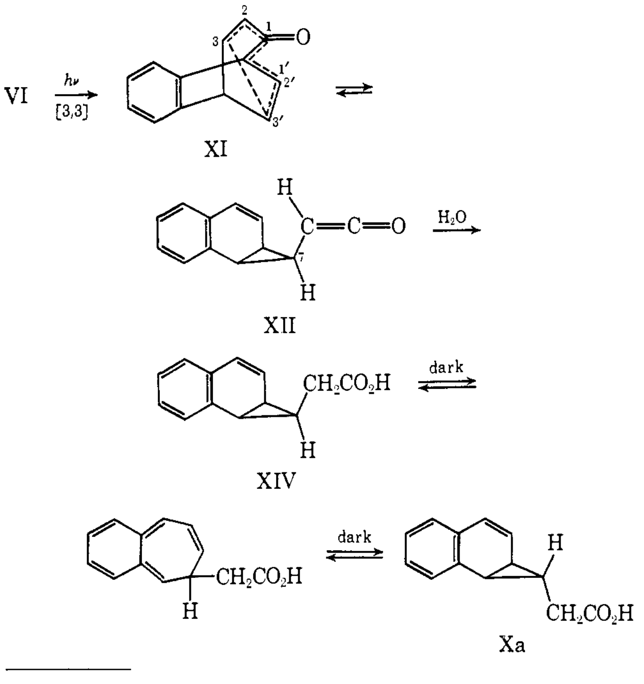


IXa, R = COOH
b, R = $COCHN_2$
c, R = CH═C═O



Xa, R = H
b, R = $CH_3$

Formation of photoacid Xa, its *exo* stereochemistry secured both by synthesis and the 4-Hz vicinal coupling[9] between the C-7 proton and each of its two *trans* neighbors, may be explained by an initial [3,3] photorearrangement (*cf.* XI) to a cyclopropylketene of gross structure XII, followed by hydration.[10] The *exo* stereochemistry could arise from (a) nonstereospecific formation of the cyclopropane ring during the rearrangement, (b) stereospecific inversion at C-7 of XII during rearrangement,[11] (c) a secondary photoreaction producing inversion of an initially formed *endo* intermediate, or (d) a secondary thermal reaction effecting inversion of an initially formed *endo* intermediate. Alternative d is in fact correct, since photolysis of VI at 0° followed by rapid crystallization of the reaction product gives a new $C_{13}H_{12}O_2$ photoacid, mp 79–80°, in 40% yield. This second acid is recognized as the unstable *endo* compound XIV on the basis of its nmr spectrum[12] and its conversion, on standing in solution in the dark for several days, to an equilibrium mixture containing 60% of the *exo* acid Xa. The thermal inversion process XIV → Xa has exact analogy[13] and permits formulation of the over-all reaction sequence as follows.



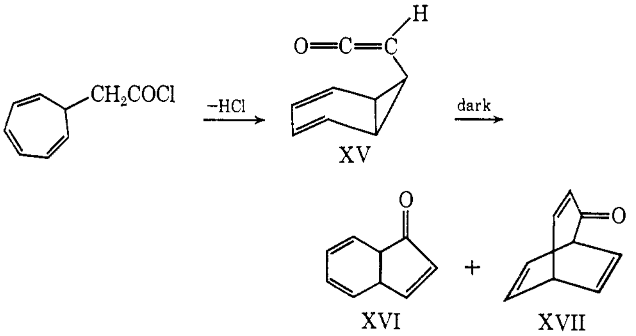
XI

XII

XIV

Xa

There remains, however, the intriguing question of the origin of the ketonic photoisomer VII. Goldstein and Odell have proposed that the ketene XV rearranges thermally to approximately equal amounts of the dihydroindenone XVI and the bicyclononatrienone XVII.[14] On this basis one might anticipate that our photoketone VII could arise from the cyclopropylketene XII already implicated in photoacid formation.



XV

XVI

XVII

Despite this apparent analogy, two key observations preclude the intermediacy of ketene XII as a significant precursor of photoketone VII. First, independent generation of *exo* ketene IXc from the acid chloride of Xa at 80° produces appreciable amounts of starting ketone VI (presumably *via* XII), but not even a trace of ketones VII or VIII. Second, the effect of methanol concentration on the rates of product formation in the photolysis of ketone VI (Table I) clearly shows that the rate of appearance of VII (by glpc) is independent of nucleophile concentration; it is therefore not formed from ketene XII in competition with methanolysis of the latter.

**Table I.** Relative Rates of Product Formation in Photolysis of VI[15]

| Solvent composition | VII formed, % | Xb formed, % | VI remaining, % |
|---|---|---|---|
| 0% $CH_3OH$–100% $CH_3CN$ | 2.9 | | 97 |
| 10% $CH_3OH$–90% $CH_3CN$ | 2.6 | 4.2 | 86 |
| 50% $CH_3OH$–50% $CH_3CN$ | 3.4 | 26 | 57 |
| 90% $CH_3OH$–10% $CH_3CN$ | 2.6 ± 0.5 | 28 ± 2 | 41 ± 5 |

We conclude from the above data that the chemistry of excited ketone VI *involves two distinct and competitive primary processes.* The more rapid of these is stereospecific [3,3] rearrangement to ketene XII which may be trapped by nucleophiles but otherwise reverts rapidly to ketone VI at room temperature. The minor pathway, approximately one-tenth as fast as the above, is a [1,3] acyl migration directly producing photoketone VII. Sensitized irradiations in which benzophenone captures *ca.* 90% of the light sharply retard the appearance of both VII and IXb and lead instead to the rapid formation of a new photoproduct, isomeric with VI.

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(9) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(10) The ketene XII has been observed in the low-temperature photolysis of ketone VI as carried out by O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6856 (1969). We are indebted to Professor Chapman for sharing this information with us prior to publication.

(11) J. A. Berson and G. L. Nelson, *ibid.*, **89**, 5503 (1967).

(12) Nmr spectrum (in $CDCl_3$) of *endo* acid XIV: δ 1.7–2.0 (1 H, m), 1.88 (2 H, d), 2.0–2.3 (1 H, m), 2.55 (1 H, q), 6.12 (1 H, q, $J$ = 10, 5 Hz), 6.55 (1 H, d, $J$ = 10 Hz), 7.2 (4 H, m), 10.8 (1 H, s); compare the *exo* acid Xa: δ 0.45 (1 H, m), 1.9 (1 H, m), 2.33 (1 H, q, $J$ = 6, 4 Hz), 2.53 (2 H, d, $J$ = 7 Hz), 6.31 (2 H, AB), 7.3 (4 H, m), 10.6 (1 H, s). A mixture melting point of the *endo* and *exo* acids was 67–70°.

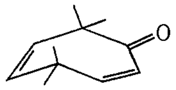
(13) E. Vogel, D. Wendisch, and W. D. Roth, *Angew. Chem.*, **76**, 432 (1964).

(14) M. J. Goldstein and B. G. Odell, *J. Am. Chem. Soc.*, **89**, 6356 (1967).

(15) Photolyses were carried out using 3.3% solutions of ketone VI each containing 3% ethyl phenylacetate as internal standard for glpc. Samples were irradiated for 30 min in Pyrex tubes ($N_2$ atmosphere) placed equidistant from a 140-W medium-pressure source. Aliquots of 5 μl from each were mixed with 2 μl of triethylamine under standard conditions known to convert all of VII to VIII, then analyzed by glpc using 6 ft × $^1/_8$ in. columns (10% Ucon on Chromosorb W 98) at 205°.

These data clearly point to singlet excited VI as the principal precursor to both the 1,3 and 3,3 migration processes.

Preliminary results paralleling those of Table I indicate that the photochemistry of the simple bicyclononatrienone XVII also proceeds through competitive [3,3] and [1,3] sigmatropic rearrangements, the former predominating. An extension of this study to other "homocyclohexadienones" (XVIII) is in progress.


XVIII

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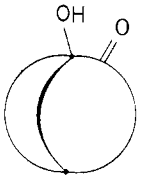
*Received August 13, 1969*

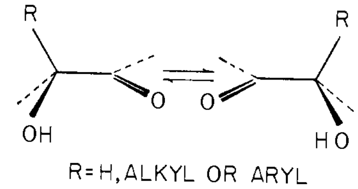
## Bridgehead Ketols

*Sir:*

We wish to draw attention to a class of compounds (bridgehead ketols,**1**) that offers a variety of novel ways to enrich our knowledge and understanding of skeletal rearrangements in bridged molecules. This communication (a) points out some of the special features of the bridgehead $\alpha$-ketol unit, (b) reports the synthesis and characterization of the norbornyl representative **8**, which is a key member of the class, and (c) presents evidence that **8** undergoes the essential degenerate alkali-induced rearrangement that underscores the utility of these compounds for mechanistic studies.

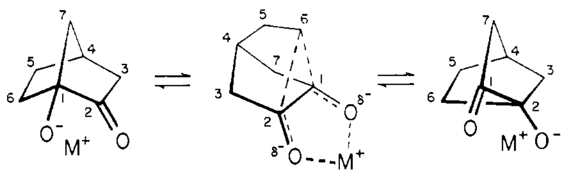


1



2

Isomerizations of $\alpha$-hydroxy carbonyl compounds (see **2**) can often be induced by acidic and basic reagents and are well documented, especially in the steroid field.[1] If the ketol unit were at a bridgehead (**1**) of a suitably bridged system, the rearrangement could be degenerate, and the midway stage would have geometry like that in Wagner–Meerwein shifts. Equation 1 illustrates the interconversion of the norbornyl analog *dextro*-**3** $\leftrightarrows$ *levo*-**3** by alkali (M = cation). Whether the delocalized species *meso*-**3** is a transition state or an intermediate is as pertinent a consideration in this *anionic* rearrangement as it is in its cationic counterpart, the norbornyl cation. However, unlike the elusive cation, which scrambles by hydrogen shifts, the anion **3** should be largely stable in alkaline medium, and complications due to hydrogen scrambling are precluded by involvement of the two oxygens.[2]



(1)

dextro-3 meso-3 levo-3

Nmr and X-ray crystallographic investigations of metal salts (or perhaps even metaloid complexes[3]) could be used to learn whether classical (*e.g.*, *dextro*-**3**) or nonclassical (*e.g.*, *meso*-**3**) structures prevail. Various $\pi$ routes and $\Delta$ routes[4] to **3** can be envisaged, as can structural modifications (*e.g.*, replacement of oxygen by other heteroatoms) that might enhance the relative stability of the delocalized form. Since ways are available[5] for conversion of HOR to ·OR, bridgehead ketols are also potentially useful to study rearrangements, electron delocalization, etc., in alkoxy radicals. In addition, the 1,2-dioxygenated array can be used to set up specialized features in *cationic* shifts. For example, products and rates in solvolyses of *exo* and *endo* C-2 brosylates with an oxygen function at C-1 (*e.g.*, OH, OR, etc.) are of high interest in their own right and will be reported separately. The accompanying communication reveals still a different application in an nmr study of equilibrating tertiary cations.[6]

Our synthetic scheme to ketol **8** involved hydrolysis of 2-bromonorbornane-1-carboxylic acid (**4**)[7] in acid and oxidation of the crude hydroxy acids with Jones reagent. The derived keto acid **5** ($C_8H_{10}O_3$; mp 128.5–129.5°;

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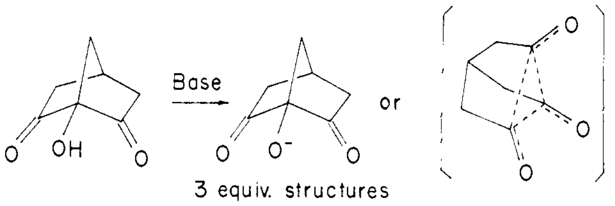
[1] (a) For leading references to steroidal examples, see a review by N. L. Wendler in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 16; (b) Y. Mazur and M. Nussim, *Tetrahedron Letters*, 817 (1961); (c) H. O. House and H. W. Thompson, *J. Org. Chem.*, 28, 164 (1963); (d) D. Y. Curtin and S. Leskowitz, *J. Amer. Chem. Soc.*, 73, 2633 (1951); (e) J. F. Eastham, J. E. Huffaker, V. F. Ramen, and C. J. Collins, *ibid.*, 78, 4323 (1956); (f) M. J. Frearson and D. M. Brown, *J. Chem. Soc., C*, 2909 (1968).

[2] Intriguing variants are "sesquiketols" (*e.g.*, i) in which the corresponding alkoxide could adopt three degenerate structures (ii), each with a plane of symmetry, or a single mesomeric structure with $C_{3v}$ symmetry (iii).



i ii iii

[3] Ordinarily $\alpha$-hydroxy ketones do not form isolable metal chelates, but the stability of cupric tropolone and of chelates of dithiotropolone indicate that specialized features can alter this: J. M. Robertson, *J. Chem. Soc.*, 1222 (1951); C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, 90, 6884 (1968).

[4] A. Nickon and G. D. Pandit, *Tetrahedron Letters*, 3663 (1968).

[5] For leading references see: (a) A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, 17, 35 (1962); (b) M. Akhtar, P. Hunt, and P. B. Dewhurst, *J. Amer. Chem. Soc.*, 87, 1807 (1965); (c) A. Padwa, *Tetrahedron Letters*, 3465 (1964); (d) D. B. Denney and J. W. Hanifin, Jr., *J. Org. Chem.*, 29, 732 (1964); (e) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *J. Amer. Chem. Soc.*, 83, 2196 (1961); (f) D. Rosenthal, C. F. Lefler, and M. E. Wall, *Tetrahedron Letters*, 3203 (1965); (g) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957; (h) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

[6] A. Nickon and Y.-i Lin, *J. Amer. Chem. Soc.*, 91, 6861 (1969).

[7] (a) W. Boehme, *ibid.*, 81, 2762 (1959); (b) H. Kwart and G. Null, *ibid.*, 81, 2765 (1959).