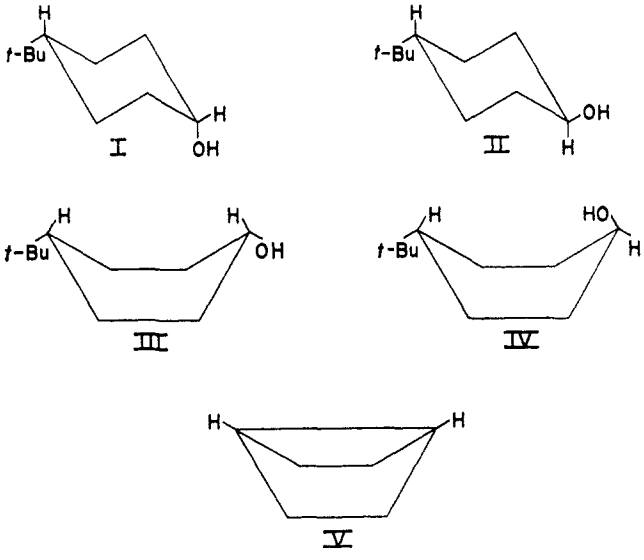
Shannon, *et al.*,[8] have suggested the ion resulting from the 1,4 elimination may be related to the [2.2.0]bicyclohexane system (V). If this is so, and if 1,4 elimination can occur in the 4-*t*-butylcyclohexanol system, then the simple expedient of inverting the conformation of the ion (IIa) derived from the *trans* isomer (II) into the boat symmetry (IVa) would enable the 1,4 elimination of water to occur quite readily. This elimination would be far less likely to occur in the *cis* isomer (IIIa). Further evidence supporting this hypothesis follows from the work of Srinivasan,[9] who obtained the mass spectrum of [2.2.0]bicyclohexane and found major peaks at M, M − 15, M − 28, M − 41, and M − 43. If it is correct that an ion related to [2.2.0]bicyclohexane is an intermediate in the fragmentation of the *trans* isomer and not in the case of the *cis* isomer, then we should expect to see prominent peaks in the spectrum of the *trans* isomer at mass numbers 138, 123, 110, 97, and 95. These have been indicated by dotted lines in Figure 1, from which it can be seen that peaks occur as required. The fact that this rationale involves the suggestion that the *trans* isomer must assume the boat conformation for at least some excited states of its ion does not appear unreasonable to us in view of the energetics of the photoionization process.



Acknowledgment. It is a pleasure for both of us to acknowledge financial assistance from the National Research Council of Canada.

(9) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

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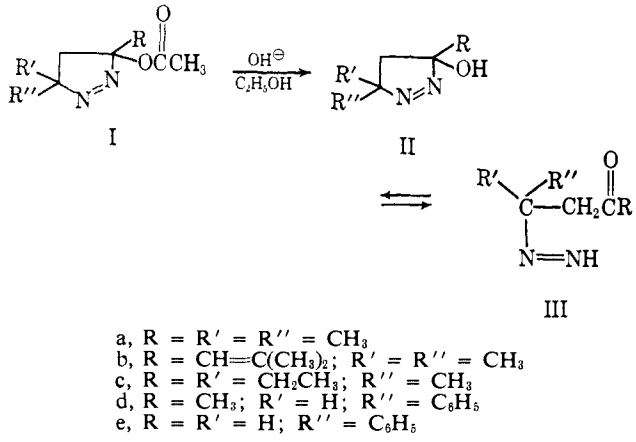
Received May 23, 1966

A Carbanion Rearrangement *via* a Homoenolate Ion

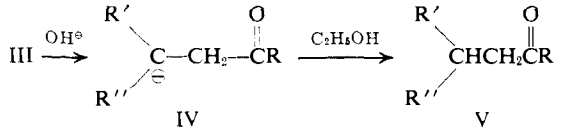
Sir:

The intervention of cyclopropanol intermediates or homoenolate ions in some ketone reactions under alkaline conditions has been reported recently.[1] During an investigation of the hydrolysis of 3-acetoxy-Δ^1-pyrazolines (I)[2] we observed a carbon skeleton rearrangement that appears to involve the intermediate formation of a homoenolate ion. The alkaline hydrolysis of these pyrazolines was examined with a view to obtaining the corresponding alcohol II, the intramolecular adduct III of a ketone, and an alkyldiimide, for further study. In no cases were such compounds detected, but efforts are still being made to isolate them.



a, R = R′ = R″ = CH_3
b, R = $CH{=}C(CH_3)_2$; R′ = R″ = CH_3
c, R = R′ = CH_2CH_3; R″ = CH_3
d, R = CH_3; R′ = H; R″ = C_6H_5
e, R = R′ = H; R″ = C_6H_5

It would be expected on the basis of the currently accepted mode of decomposition of diimides in alkaline solution[3] that intermediate III would lose nitrogen to produce carbanion IV and ultimately ketone V. In



fact, however, the major product of alkaline hydrolysis of Ia was pinacolone along with a lesser amount of the expected methyl isobutyl ketone. Hydrolysis of Ib yielded only 2,5,5-trimethyl-2-hexen-4-one, a product of carbon skeleton rearrangement, and none of the isobutyl ketone Vb. Hydrolysis of Ic yielded ethyl *t*-amyl ketone as a major product along with a small amount of the expected ketone Vc. Attempted hydrolyses of Id and Ie did not lead to nitrogen evolution but rather to loss of acetic acid and to the formation of the corresponding pyrazoles.

It is believed that these rearrangements may be rationalized by the mechanism shown in Scheme I.[4] In support of this scheme is the fact that hydrolysis of 1,2,2-trimethylcyclopropyl acetate yields a mixture consisting of 90% pinacolone and 10% methyl isobutyl ketone,[5] and hydrolysis of 1-isobutenyl-2,2-dimethylcyclopropyl acetate yields only 2,5,5-trimethyl-2-hexen-4-one. DePuy[6] has reported that cyclopropanols open in base to give the product derived from the more stable carbanion.

(1) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965), and prior references; A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966).

(2) J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964).

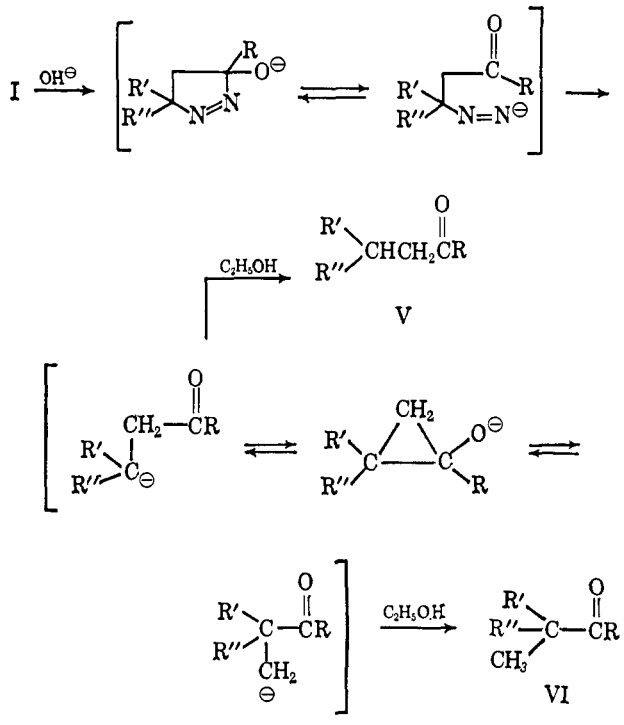
(3) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., p 159.

(4) The equilibria represented in this scheme are written for the purpose of allowing the reader to follow the rearrangement rather than to imply anything specific about the lifetimes or individuality of the structures displayed.

(5) Interestingly, acid hydrolysis of Ia yielded exclusively methyl isobutyl ketone suggesting that, as expected, the lifetime of the carbanionic species in acid solution is very short.

(6) C. H. DePuy, Abstracts, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 1963, p. 31; C. H. DePuy and F. W. Breitbeil, *J. Am. Chem. Soc.*, **85**, 2176 (1963).

Scheme I



Recently it was reported that the Clemmenson reduction of α,β-unsaturated ketones involves a cyclopropanol intermediate.[7] The present examples may be viewed as analogous variations of the Wolff–Kishner reduction in that the over-all process is the saturation of an α,β-unsaturated ketone. It is planned to investigate the kinetics of this hydrolysis and the utility of this reaction for the preparation of otherwise difficultly accessible ketones.

(7) B. R. Davis and P. D. Woodgate, *Chem. Commun.*, 65 (1966).

(8) This research was supported in part by a grant from the Petroleum Research Fund.

(9) National Science Foundation Undergraduate Research Participant.

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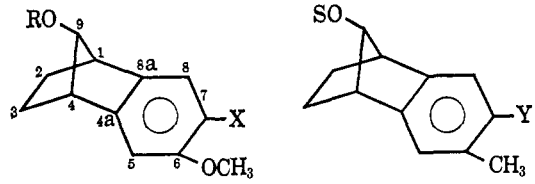
Received May 14, 1966

Acetolysis of 6,7-Dimethoxy-*anti*-9-benzonorbornenyl *p*-Bromobenzenesulfonate. Evidence for a Symmetrical Transition State[1]

Sir:

In previous papers,[2] strikingly large substituent effects observed in the acetolysis of 6-substituted *anti*-9-benzonorbornenyl *p*-bromobenzenesulfonate (k_{OCH_3}/k_{NO_2} = 3.86 × 10^5 at 77.6°) were correlated by the modified Hammett relationship, $\log(k/k_0) = \rho(\sigma + \sigma^+)$ or $\rho(\sigma_p^+ + \sigma_m^+)$, and the implications of this alternative correlation have been discussed on the basis of the idea of internal aromatic substitution and/or of the simultaneous participation from the *meta* and *para* positions of the 6 substituents. For selection between these alternative possibilities and thereby for a better understanding of whether the solvolysis of *anti*-7-norbornenyl derivatives proceeds through the formation of a symmetrical or an unsymmetrical transition state, the synthesis and the study of the solvolytic behavior of symmetrically 6,7-disubstituted *anti*-9-benzonorbornenyl *p*-bromobenzenesulfonates are desirable.

The Friedel–Crafts acylation (CH_3COCl–$AlCl_3$ in CS_2) of 6-methoxy-*anti*-9-benzonorbornenol acetate (**1**)[2a] afforded a mixture of 6-methoxy-7-acetyl-*anti*-9-benzonorbornenol acetate (**2**),[3] mp 112–113°, and its demethylated 6-methoxy-7-hydroxy-*anti*-9-benzonorbornenol acetate (**3**), mp 146–147°. The latter was converted into **2** by treatment with methyl iodide and silver oxide. The position of the acetyl group[4] was established by the nmr pattern of aromatic protons: aryl H_5 at τ 3.22 (singlet), aryl H_8 at τ 2.51 (singlet). The Baeyer–Villiger oxidation of **2** with *m*-chloroperbenzoic acid yielded the acetoxy derivative **4**, mp 138°, whose hydrolysis using lithium aluminum hydride followed by methylation of the phenolic hydroxyl group with dimethyl sulfate gave the desired 6,7-dimethoxy-*anti*-9-benzonorbornenol (**5**), mp 121–122°. The structure was confirmed by the nmr spectrum: two aryl H at τ 3.23 as a singlet, six methyl H at τ 6.16 as a singlet, one C_9 H at τ ~6.2 (overlapped with methyl H), two C_1,C_4 H at τ 6.95 as a multiplet, two C_2,C_3 *exo*-H around τ 7.8–8.1, and two C_2,C_3 *endo*-H around τ 8.7–9.0.



1, R = Ac; X = H
2, R = Ac; X = Ac
3, R = Ac; X = OH
4, R = Ac; X = AcO
5, R = H; X = OCH_3
6, R = Bs; X = OCH_3

7, S = Ac; Y = H
8, S = H; Y = CH_3
9, S = Bs; Y = CH_3

The chloromethylation (HCHO–HCl–CH_3COOH) of 6-methyl-*anti*-9-benzonorbornenyl acetate (**7**)[2a] followed by lithium aluminum hydride reduction afforded 6,7-dimethyl-*anti*-9-benzonorbornenol (**8**), mp 129.5–130.5°. The structure was established by the nmr spectrum: two aryl H at τ 3.18 as a singlet, one C_9 H at τ 6.30 as a multiplet, two C_1,C_4 H at τ 7.02 as a multiplet, six methyl H at τ 7.80 as a singlet, two C_2,C_3 *exo*-H around τ 7.8–8.1, and two C_2,C_3 *endo*-H around τ 8.8–9.1. The brosylates **6**, mp 147–148°, and **9**, mp 135.5–136°, were prepared from **5** and **8**, respectively, by a standard method.

The rates of acetolyses of **6** and **9** were carried out in glacial acetic acid containing 1 equiv of sodium acetate and are summarized in Table I, together with the rates of relevant compounds. It is clearly indicated that one CH_3O (or CH_3) substituent in the 6 position increases the rate by a factor of 54 (or 5.7) and two CH_3O (or CH_3) substituents in the symmetrical 6 or 7 positions increase the rate by a factor of 3000 (or 36), approximately the square of the value for the one substituent. Thus it was proved that, when $(\sigma_p^+ + \sigma_m^+)$ was used for the disubstituted compounds, all the rate data are

(1) The numbering used before[2] is replaced as shown in the formula, adapting the IUPAC rule.

(2) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964); (b) H. Tanida, *ibid.*, **85**, 1703 (1963).

(3) Satisfactory analyses were obtained for all compounds described.

(4) Exclusive β orientation in the aromatic substitution of benzonorbornene derivatives was observed; see H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965).