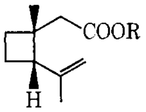
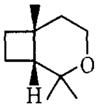
and 4.84 (broad s, two vinylic *H*), and 10.72 (COO*H*) contaminated by 3% of the undesired *trans* isomer as shown by gc analysis[8a] of the derived methyl esters **17**. Completion of the synthesis by reduction of **16** or **17** with sodium dihydridobis(2-methoxyethoxy)aluminate[17] in benzene–ether gave, after purification by preparative gc,[8a] the racemic pheromone **1**: bp bath 50° (12 mm); ir (CCl_4) 3610 (OH), 3075, 1645, and 892 cm^{-1} ($C{=}CH_2$); molecular ion found[13b] at *m/e* 154.13568 (calcd 154.13576). The nmr spectrum (CCl_4) of **1** showed resonances at 1.18 (s, 1-C*H*$_3$), 1.67 (broad s, vinylic C*H*$_3$), 1.88 (s, O*H*), 2.53 (t, J = 8.5, allylic *H*), 3.56 (t, J = 7, C*H*$_2$OH), 4.60 and 4.80 (broad s, two vinylic *H*) and established identity[18] with the natural product. Proof of the *cis* relationship (by reconnection) of side chains in **1** was obtained by treating[19] a 9:1 *cis–trans* isomer mixture of **1** with mercuric acetate (1 equiv) in dry tetrahydrofuran followed by aqueous alkaline sodium borohydride. The product was predominantly the cyclic ether[8c] **18** [nmr 1.02, 1.15, and 1.17 (three s, quaternary methyls) and 3.60 (m, C*H*$_2$O); molecular ion found[13b] at *m/e* 154.13581 (calcd 154.13576)], together with unchanged alcohol *trans* **1**, whose gc retention time[8b] (55.2 min) at 135° differed from that (54 min) of the pheromone **1**.



16, R = H
17, R = CH_3



18

When combined by Drs. D. D. Hardee and R. C. Gueldner (U. S. D. A., Boll Weevil Research Laboratory) with compounds **2**, **3**, and **4** for bioassay, the synthetic pheromone **1** showed activity in laboratory tests essentially identical with that of the natural product. We are most grateful for this determination.

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(17) J. Vít, B. Čåsenský, J. Machåček, French Patent 1,515,582 (1967)

(18) Nmr spectra (CCl_4) of the natural product **1**, presented[5] by Dr. J. H. Tumlinson, show resonances at 1.22 (s), 1.72 (s), 2.59 (s, O*H*), 2.60 (broad t), 3.63 (t), 4.71, and 4.88 ppm. In contrast the *trans* isomer shows the quaternary methyl at 0.95 ppm.

(19) *Cf.* H. C. Brown and M. Rei, *J. Amer. Chem. Soc.*, **91**, 5646 (1969).

(20) Zoëcon Postdoctoral Fellow, 1968–1969.

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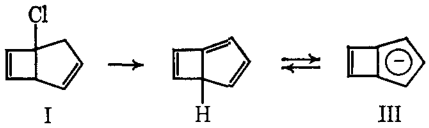
Antiaromatic Destabilization of Cyclobutadienocyclopentadienyl Anion

Sir:

We have reported[1] the observation that dehydrochlorination of I with KO-*t*-Bu produces a reactive triene II which dimerizes rapidly. We were also able to detect the equilibration of II with its anion III by observing deuterium exchange into II, producing dimers of II-d_1. It was originally suggested that a single Diels–Alder dimer was formed, but quickly discovered and reported[2] that a mixture of two dimers was actually formed by 2 + 2 addition of the strained double bond. Bauld has also shown[3] that this mixture of dimers is produced on generation of triene II, although curiously he did not observe deuterium exchange in II under our conditions. Cava has reported the preparation of a benzo derivative of III in solution.[4]



I II III

The pK_a of II is of interest since, of the five normal resonance structures for cyclopentadienyl anion, two of them in III would also have a cyclobutadiene ring structure. Thus if cyclobutadiene is "antiaromatic," *i.e.*, conjugatively destabilized,[5] this should lead to a high pK_a for II by comparison with cyclopentadiene. We wish to report that we have succeeded in preparing a solution of III, and have also determined an approximate pK_a for II which reveals strong destabilization in III by the cyclobutadiene ring fusion.

A solution of anion III was obtained by adding 200 mg (1.6 mmol) of I dropwise to 4 mmol of lithium dicyclohexylamide and 17 mmol of tetramethylethylenediamine in 25 ml of tetrahydrofuran at −75°. After brief warming to −20° the solution was cooled again to −75° and quenched[6] with D_2O, then acetic acid. A mixture of 40 mg of undeuterated I and 40 mg of the dimers derived from II was obtained. By nmr integration of the signal[1,3] at δ 6.4, the dimers are derived from II-d_1 (the illustrated H replaced by D) with less than 10% from II-d_0. Thus in this strongly basic medium II exists as the anion III.

An approximate pK_a of II was determined by attempted equilibration with hydrocarbons of known acidity. Thus, to the solution of III prepared as above was added 1 equiv of triphenylmethane (pK_a = 33).[7] After 5 min at −75°, the red color of triphenylmethyl anion did not appear and quenching with D_2O, as above, afforded the dimers of II-d_1 and undeuterated triphenylmethane. By contrast, equilibration of the solution of III with fluorene (pK_a = 25)[7] afforded fluorene-d_1 (by nmr integration) and undeuterated dimers of II. With xanthene (pK_a = 29)[7] the high reactivity of II caused major difficulties. Thus 250 mg of I was converted to the solution of anion III as described above and 354 mg (1 equiv) of xanthene was added. After equilibration for 10 min at −75°, quenching afforded only 7 mg of the dimers of II, and only 40 mg of recovered xanthene. With 5-min equilibration, 15 mg of the II dimers was obtained. However, in both experiments

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(1) R. Breslow, W. Washburn, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 196 (1969).

(2) *Cf.* footnote 6 of M. P. Cava, K. Narasimhan, W. Zieger, L. J. Radonovich, and M. D. Glich, *ibid.*, **91**, 2378 (1969).

(3) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *ibid.*, **91**, 2787 (1969).

(4) (a) See Cava, *et al.*, ref 2; (b) in unpublished work, we have detected the other possible benzo derivative of III, 1,2-cyclobutadienoindenyl anion, by a procedure similar to that in ref 1.

(5) *Cf.* R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(6) Although carbanion equilibria may be disturbed during quenching in kinetically active solvents such as dimethyl sulfoxide, control studies such as those reported by R. Breslow and E. Mohacsi (*ibid.*, **85**, 431 (1963)) show that quenching with D_2O in solvents such as those used in the present study is a reliable assay for carbanion equilibria.

(7) These values are based on McEwen's acidity scale. *Cf.* D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 4.

the II dimers and recovered xanthene both indicated, by nmr, *ca.* 50% monodeuteration of II and of xanthene. These data suggest that the pK_a is near that of xanthene (~29).

We have directly determined the pK_a of cyclopentadiene in this medium relative to *t*-butyl alcohol ($pK_a = 19.0$)[7] by observing the intensity of the nmr spectrum of cyclopentadienyl anion as a function of *t*-butyl alcohol. From the relative concentration of *t*-butyl alcohol required to reduce the signal of the anion to half-height, the pK_a of cyclopentadiene is 18.2 ± 0.2 in the medium at 35°.

Thus the effect of the fused cyclobutadiene ring in III is to raise the pK_a of the cyclopentadiene moiety by *ca.* 11 units. This relative destabilization of III, by *ca.* 15 kcal/mol, probably contains some contribution from increased strain. However, it is also consistent with the hypothesis that the cyclobutadienoid resonance forms of III are appreciably antiaromatic.[8]

(8) Support of this work by the National Institutes of Health is gratefully acknowledged. These data were first reported at the National Organic Chemistry Symposium, Salt Lake City, Utah, 1969.

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Cuprous Complexes of Phenyldiazene

Sir:

Monosubstituted diazenes, which are exceedingly reactive and have defied isolation, have recently attracted considerable attention.[1] The work of Diels and Koll[2] has demonstrated the existence of complexes of the more stable 1,2-disubstituted diazenes with cuprous halides. These complexes, with the general constitution $(RN{=}NR)(CuX)_n$, may be formed either by treating a cuprous halide with the diazene or by the redox reaction between a cupric halide and a suitable hydrazine. An X-ray crystallographic study of a representative complex, $(CH_3N{=}NCH_3)Cu_2Cl_2$, has shown[3] that the compound consists of infinite chains of copper and chlorine atoms with the copper coordinated, roughly tetrahedrally, by three chlorine atoms in the chain and by a nitrogen lone pair from a diazene. The *trans*-diazene moiety bridges two cuprous chloride chains with the nitrogen atoms coordinated to copper atoms of two adjacent chains. In accord with their polymeric nature, compounds of this type have no true solubility in noncomplexing media. Since diazene complexes of this type may be prepared directly from a hydrazine without prior formation of the diazene and since the properties of these complexes are well established, we have endeavored to prepare similar complexes of the less stable monosubstituted diazenes.[4]

The addition of phenylhydrazine to an aqueous solution of cupric chloride produces a red-brown, somewhat air-sensitive complex, **1**, with the stoichiometry $(C_6H_5N{=}NH)Cu_4Cl_4$. A similar bromo complex is obtained analogously from cupric bromide. These complexes resemble other cuprous–diazene complexes. They exhibit no true solubility. Reaction of **1** with various Lewis bases results in the complete displacement of the diazene and the formation of Cu(I) complexes. For example, the reaction with dipyridyl produces $Cu(dipy)_2^+$ which can be isolated as the tetraphenylborate salt. In accord with its formulation as a cuprous complex, **1** is diamagnetic. The electronic spectrum obtained from a hydrocarbon mull of **1** shows a band at 455 nm; this is the region in which other cuprous–diazene complexes absorb.

The infrared spectrum of **1** is indicative of the presence of phenyldiazene. Only a single sharp band at 3130 cm^{-1} is observed in the region expected for the N–H stretching vibration. This vibration is shifted to 2320 cm^{-1} in the N-deuterated analog, which was prepared from $C_6H_5NDND_2$ in deuterium oxide. In contrast, authentic cuprous–phenylhydrazine complexes exhibit, as expected, several infrared bands in the N–H stretching region. For example, white $C_6H_5NHNH_2 \cdot CuI$, **2**, prepared by treating an aqueous potassium iodide solution of cuprous iodide with phenylhydrazine, has infrared absorptions at 3310, 3290, 3230, and 3150 cm^{-1}. It has not been possible to unambiguously assign a vibrational band to the N=N stretching frequency. Four bands at 1490, 1470, 1450, and 1420 cm^{-1} occur in the region where this vibration is expected.[5] Similar difficulties have been encountered in attempting to assign the N=N stretching vibration in 1,2-diphenyldiazene complexes.[5]

Pyrolysis of **1** produces detectable quantities of phenyldiazene in the vapor phase. The mass spectrum of the volatile species obtained from **1** using direct insertion techniques with a source temperature of 120° exhibits an intense peak at *m/e* 106.0531 (calcd for $C_6H_6N_2$, 106.0531). For the corresponding N-deuterated complex the most intense peak in this region occurs at *m/e* 107.6594 (calcd for $C_6H_5DN_2$, 107.6594). These peaks are not caused by fragmentation or pyrolysis of phenylhydrazine in either a complexed or free state. The relative intensities of the peaks at *m/e* 106 and 108 ($C_6H_5N_2H_3$) in the spectrum derived from **1** are in the ratio 35:1, whereas the mass spectrum obtained from the phenylhydrazine complex **2** under identical conditions exhibits peaks at *m/e* 106 and 108 in the ratio 1:15. Similarly in the mass spectrum of phenylhydrazine these peaks are in the ratio 1:17.

The complex **1** can be used as a convenient means of preparing acetonitrile solutions of phenyldiazene. It has been reported that phenyldiazene can be codistilled

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(1) (a) Phenyldiazene: P.-k. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, 90, 2354, 2362, 2367 (1968); (b) substituted aryldiazenes: E. M. Kosower, P.-k. C. Huang, and T. Tsuji, *ibid.*, 91, 2325 (1969); (c) methyldiazene: M. N. Ackermann, J. L. Ellenson, and D. H. Robison, *ibid.*, 90, 7173 (1968); (d) *t*-butyldiazene: P.-k. C. Huang and E. M. Kosower, *ibid.*, 89, 3911 (1967); (e) alkenyldiazenes: T. Tsuji and E. M. Kosower, *ibid.*, 91, 3375 (1969).

(2) O. Diels and W. Koll, *Justus Liebigs Ann. Chem.*, 443, 262 (1925).

(3) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 13, 28 (1960).

(4) Some examples of monosubstituted diazene complexes are known. The reaction of benzenediazonium ion with a platinum hydride complex produces a platinum complex of phenyldiazene: G. W. Parshall, *J. Amer. Chem. Soc.*, 89, 1822 (1967); 87, 2133 (1965). Complexes which may be considered as containing deprotonated diazenes have also been reported: R. B. King and M. B. Bisnette, *Inorg. Chem.*, 5, 300 (1966); G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967). Spectroscopic and other evidence for the interaction of phenyldiazene and diazene (HN=NH) with ferroporphyrin and ferroheme proteins has been published: P.-k. C. Huang and E. M. Kosower *Biochim. Biophys. Acta*, 165, 483 (1868); H. A. Itano and E. A. Robinson, *J. Amer. Chem. Soc.*, 83, 3339 (1961); W. G. Hanstein, J. B. Lett, C. E. McKenna, and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S.*, 58, 1314 (1967).

(5) A. L. Balch and D. Petredis, *Inorg. Chem.*, 8, 2247 (1969).