of the zinc ion produced by an interaction of the spins on the ligand with an excited state of the zinc ion.

Another exception is that in all cases, within the experimental error (the maximum value is ±3%), the splittings for the beryllium and corresponding magnesium compound are the same. This may imply that in the beryllium chelates the ligands are kept apart, not by the size of the cation, but by the repulsion between the ligands.

In addition to presenting many possibilities for the study of electronic interactions, the compounds described here may be useful in synthetic procedures where it is desirable to have pairs of electrons available for reduction purposes.

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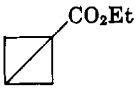
RECEIVED JUNE 28, 1963

Bicyclobutane

Sir:

Interest in the chemical and physical properties of highly strained molecules induced us to attempt the synthesis of the simplest bicyclic compound, [1.1.0]-bicyclobutane (**1**). Although two substances (**2**[1] and **3**[2]) possessing the carbon skeleton of bicyclobutane have appeared in the literature, for reasons of symmetry and simplicity the parent substance was uniquely suited for certain studies.

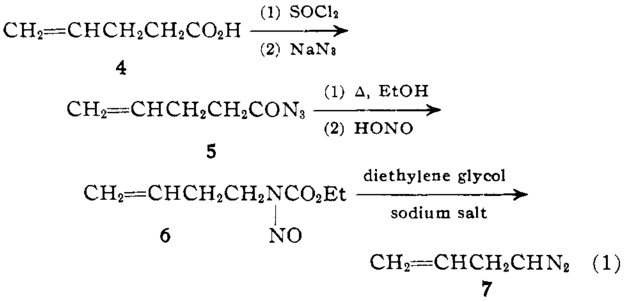

1



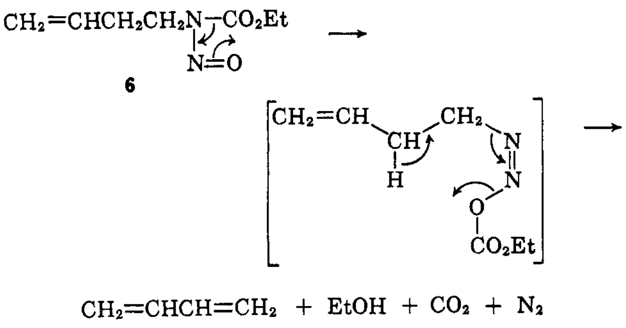
2


3

We hoped that intramolecular addition of a divalent carbon atom to an olefinic double bond, a process known to be successful when the reactive sites are well separated,[3] could lead to the highly strained system. Allyldiazomethane (**7**) was an appropriate substrate for this attempt. It was prepared from allylacetic acid (**4**) *via* the acid chloride, the azide (**5**), allylcarbinylurethan (b.p. 62–64° (1.5 mm.); infrared $\lambda_{\max}^{CHCl_3}$ 2.90, 5.84, 6.10 μ; *Anal.* Found: C, 58.61, H, 9.05, N, 9.84), and N-nitrosoallylcarbinylurethan (**6**) (eq. 1).[4] Thermal decomposition of the nitroso compound **6** at temperatures above 150° gave butadiene, ethanol, carbon dioxide, and nitrogen as the only products detectable by v.p.c. A possible mechanism for the fragmentation is shown at the top of the next column.[5]



$$\underset{\mathbf{4}}{CH_2{=}CHCH_2CH_2CO_2H} \xrightarrow[(2)\ NaN_3]{(1)\ SOCl_2} \underset{\mathbf{5}}{CH_2{=}CHCH_2CH_2CON_3} \xrightarrow[(2)\ HONO]{(1)\ \Delta,\ EtOH} \underset{\mathbf{6}}{CH_2{=}CHCH_2CH_2\underset{NO}{\underset{|}{N}}CO_2Et} \xrightarrow[\text{sodium salt}]{\text{diethylene glycol}} \underset{\mathbf{7}}{CH_2{=}CHCH_2CHN_2} \quad (1)$$



6

Because of its lability the nitroso compound was transformed without purification into allyldiazomethane by rapid addition to a vigorously stirred solution of excess diethylene glycol sodium salt in diethylene glycol at 0°. The system was maintained at a low pressure in order that the diazoalkane distil as it was formed into a trap cooled by Dry Ice. After three additional distillations in the cold, the orange diazo compound was stored in heptane solution at −78°.

Aliquots of the allyldiazomethane solution were added to acetic acid–heptane and the excess acid was titrated with methanolic sodium methoxide. Vapor phase chromatography indicated that butadiene as well as allylcarbinyl acetate was formed in the reaction with acetic acid[6]; the diene:ester ratio was markedly dependent upon the acid concentration. It was necessary to correct the titrimetric assay slightly for diene formation since this reaction consumes no acid. The yield of allyldiazomethane was calculated to be approximately 30% from the nitrosourethan, 16% from allylacetic acid.

A 5% solution of the diazo compound in heptane was photolyzed in Pyrex at −78° using a Hanovia 450-watt Type L lamp. The volume of nitrogen evolved was close to the theoretical, and v.p.c. analysis of the now colorless solution revealed in addition to heptane two compounds in the ratio 5:1. Not surprisingly, the major component was identified as butadiene by n.m.r. and mass spectral comparison with an authentic sample. Deuterium labeling studies demonstrated that most, but not all, of the butadiene arose by 1,2-hydrogen migration.

The striking similarity in mass spectra of the major and minor photolysis products established that the latter was isomeric with butadiene. Cyclobutene and methylenecyclopropane, both mechanistically plausible isomers, had in common with butadiene slightly shorter retention times on Ucon Polar than that of the unknown hydrocarbon. Critical evidence was provided by the n.m.r. spectrum (CCl_4), which displayed a complex multiplet centered at 8.61 τ (relative area 2) and a "singlet" at 9.55 τ (relative area 1) that possessed fine structure under high resolution. Only the bicyclic structure for C_4H_6 is consistent with these data.

$$\underset{\mathbf{7}}{CH_2{=}CHCH_2CHN_2} \xrightarrow{h\nu} CH_2{=}CHCH{=}CH_2 +$$


1

Although the combined yield of butadiene and bicyclobutane was essentially quantitative, the content of bicyclic isomer in the photolysis mixture dropped to zero after a few days even at temperatures well below 0°, presumably as a result of radical polymerization or autoxidation. Thermal isomerization of the strained hydrocarbon to butadiene was complete within 4 min. at 150° but only slight during the same interval at 110°. At the latter temperature a small amount of cyclobutene accompanied the diene in the pyrolysate.

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[2] W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

[3] G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

[4] P. A. S. Smith, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapter 9, p. 337; W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 464.

[5] E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174 (1961).

[6] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 120–136.

Further investigation of allyldiazomethane and of bicyclobutane is in progress.

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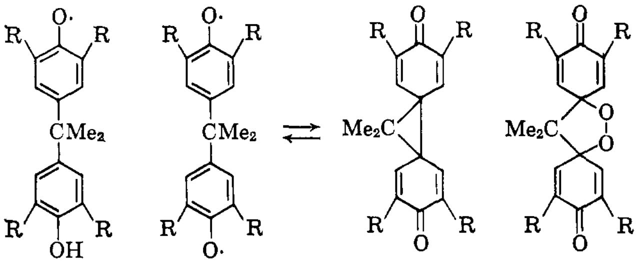
RECEIVED JUNE 3, 1963

Electronic Interactions in Biradicals. I. Reversible Bond Formation

Sir:

There is considerable interest in the chemistry of biradicals which, in some cases, may interact sufficiently to be termed triplets.[1] The synthesis of a potential triplet containing two phenoxyl radicals in a cross-conjugated system has been reported by Yang and Castro.[2] We have studied a system containing two individually stable phenoxyl radicals not connected to a single π-electron system but held together as closely as possible—bound to the same saturated carbon atom. The system we chose is derived from 2,2-bis-(3,5 di-*t*-butyl-4-hydroxyphenyl)-propane (I).[3]



II III IV V

R = *t*-butyl

Metal oxides (PbO_2, Ag_2O, MnO_2) oxidized I readily, but treatment of a benzene solution of I with aqueous alkaline $K_3Fe(CN)_6$ was most effective for preparative scale work. Evaporation of the solvent with nitrogen left brick-red needles (m.p. *ca.* 120° dec.) which could be crystallized from pentane. Iodometric titration indicated the consumption of 1.85 equivalents of HI and regenerated I (55%, crystallized). The infrared spectrum of the product was interpretable in terms of structure IV, resulting from internal bond formation in the biradical III. There was no band at 6.4 μ, the characteristic absorption of phenoxyl radicals,[4] but there was a doublet, characteristic of this type of cyclohexadienone, at 6.08 and 6.16 μ.[4] Examination of a scale model of III indicated that the *para* positions of the radicals are held close together (the internuclear distance is 2.5 Å. when the central atom is tetrahedral) and a strained bond between these centers is conceivable. A simple spirodienone of this type has been reported by Baird and Winstein.[5]

The oxidation product, IV, was stable as a solid or in an inert solvent as long as it was protected from oxygen. The solid was decolorized slowly by air and solutions of IV reacted readily with oxygen, forming an unstable addition compound. The latter is formulated as the peroxide V on the basis of its analysis (*Anal.* Calcd. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61. Found: C, 76.70; H, 9.84) and its infrared spectrum ($\lambda_{max}^{CH_2Cl_2}$ 5.97, 6.07 μ).

The oxidation of I (benzene or cyclohexane solution) also was carried out with Ag_2O or PbO_2 in a sealed, degassed system. The initially formed product was identified as the monoradical II by virtue of its e.p.r. spectrum. The major triplet splitting is attributable to the two equivalent *meta* protons (α = 1.67 gauss) with further smaller coupling to the six equivalent protons of the isopropylidene group (α = 0.38 gauss). There is no significant interaction with the adjacent unoxidized phenolic system although the optical spectrum lacks the long wave length band responsible for the blue color of 2,4,6-tri-*t*-butylphenoxyl. Further oxidation of the solution caused a marked decrease in the intensity of the e.p.r. spectrum; the addition of excess phenol I regenerated the original spectrum. These observations are readily interpretable in terms of the equilibrium I + IV $\rightleftarrows$ 2II. No e.p.r. signal attributable to biradical III was observed and there was no absorption in rigid media other than at $g = 2$.

The ultraviolet spectrum of phenol I is essentially that of a simple phenol and has a doublet maximum at 275 and 283 mμ. The optical absorption spectrum of the solution was monitored simultaneously with the e.p.r. spectrum as oxidation of the phenol progressed. Initially, a broad absorption at 325 mμ appears as well as a sharp peak at 263 mμ. As the oxidation proceeds, the latter increases in intensity while the former, which we attribute to the monoradical II, decreases. The peak at 263 mμ corresponds well with that reported for spiro(2,5)octa-(1,4)-diene-3-one by Baird and Winstein.[5] The long wave length peak tails into the visible and is responsible for the red color of the product. The variations in e.p.r. intensity as oxidation proceeded were in accord with the conclusions reached on the basis of the optical spectral data.

The intensity of the e.p.r. spectrum of II decreased as the temperature was lowered, indicating that a thermal equilibrium was present. This is the disproportionation of II into I and IV. The Curie dependence of magnetic susceptibility may be allowed for by taking intensity (I) × temperature (T) as a measure of radical concentration. An Arrhenius plot of log IT *vs.* $1/T$ over the range 25 to −56° (CH_2Cl_2 solution) was linear and gave $\Delta H = -3.7$ kcal. The low value reflects the weakness of the strained cyclopropane bond in IV.

It appears that IV is in equilibrium with biradical III on the basis of both physical and chemical evidence although III itself could not be detected. Dienone IV would not be expected to be destroyed rapidly by oxygen, but the reaction takes only a few minutes in solution at 25°. The n.m.r. spectrum of I was in accord with its assigned structure (τ scale: t-C_4H_9, 1.33; CH_3, 1.55; OH, 4.76; ArH, 6.81). In solutions of IV, however, only a single moderately broad line was observed (1.33 τ). The absence of the vinyl proton line can be explained by rapid interconversion of III and IV. The amount of monoradical II in solution was too small to permit an explanation based on hydrogen atom exchange.[6] The sharpness of the butyl line may be explained by the low spin density at this position.[7,8] The *t*-butyl proton splitting was not resolved in the e.p.r. spectrum.

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[1] See S. I. Weissman, *Ann. Rev. Phys. Chem.*, **12**, 151 (1961).

[2] N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

[3] We thank the Ethyl Corp., Detroit, Michigan, for a gift of this compound. It was prepared by butylation of the corresponding bisphenol with isobutylene and $Al(OC_6H_5)_3$. I has m.p. 155–156°. *Anal.* Found: C, 81.94; H, 10.74.

[4] E. Muller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

[5] R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

[6] R. Kreilick and S. I. Weissman, *ibid.*, **84**, 306 (1962).

[7] This phenomenon has been observed by Weissman and Kreilick in line broadening due to hydrogen atom exchange.

[8] H. McConnell and S. B. Berger, *J. Chem. Phys.*, **27**, 230 (1957).