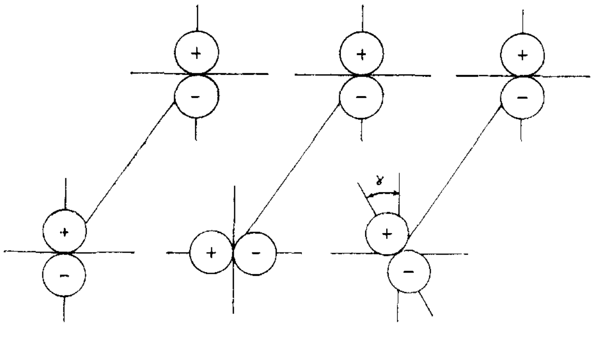
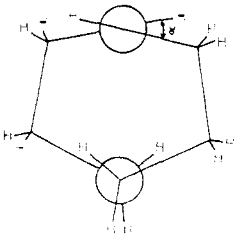
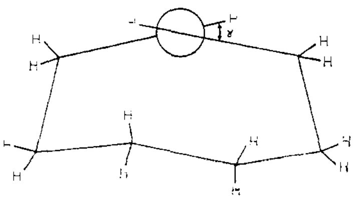


I II III

rotation $[\phi]^{29}\text{D}$ −453°, methylene chloride), where Dreiding models indicate a permanent twist of the double bond,[3] is of special interest. The Dreiding models in fact suggest two conformations of minimum angle strain which are indicated schematically in Newman projections in IV and V. The angle of twist γ may actually be slightly different for the two conformers, although the models indicate that γ is substantially the same in the two cases.



IV



V

Employing the simplest Pariser–Parr[4] wave functions for ethylene in conjunction with the Rosenfeld equation,[5] one arrives at an expression for $[\phi_t]$, the contribution of a twisted ethylenic bond to the molecular rotation

$$[\phi_t] = \frac{96\pi N_0}{hc}\,\frac{\nu^2}{\nu_0^2 - \nu^2}\,\frac{n^2 + 2}{3}\,R_{45}\sin 2\gamma \qquad (1)$$

where R_{45} is the maximal rotational strength (for a given bond distance and transition frequency ν_0) associated with $\gamma = 45°$. Here N_0 is Avogadro's number, and h, c, and n have their usual meanings. For $\gamma = 15°$, the Pariser–Parr type calculations indicate that the first ethylene π–π^* singlet transition would shift in the vapor phase from 7.6 ev. (163 mμ) to 7.38 ev. (168 mμ). Assuming a similar red shift for IV and V relative to *trans*-2-butene ($\lambda_{\text{max}}^{\text{vapor}}$ 178 mμ),[6] and assuming no further shift for the solution spectrum, one calculates from equation (1) values of $[\phi_1]^{29}\text{D}$ 395° and 404° for isoöctane and methylene chloride solvents, respectively. The optical activity so calculated is a somewhat sensitive function of angle, and for $\gamma = 20°$ one calculates $[\phi_t]^{29}\text{D}$ 551° and 564°, respectively, for the two solvents. If it is allowed that the inherent dissymmetry associated with the twist of the double bond accounts for the major portion of the observed optical activity[7] at 589 mμ, one may conclude that the absolute configuration of the (−)-enantiomer is as shown in IV and V.[8]

A direct quantitative comparison of the calculated values for $[\phi_t]_\text{D}$ with experimental values of $[\phi]_\text{D}$ is unwarranted because of the uncertainty in ν_0 and the contributions of higher lying transitions to $[\phi]_\text{D}$. Rather, a direct comparison of the calculated with the experimental rotational strength (presently lacking) for the lowest π–π^* singlet would be more appropriate. Nevertheless, if we estimate an upper limit of ± 140° due to these uncertainties,[9] we may still specify γ as equal to 17 ± 5°.

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[3] The possibility of a twisted double bond in *trans*-cycloöctene has been considered previously in connection with the interpretation of dipole moment data; N. L. Allinger, *J. Am. Chem. Soc.*, **80**, 1953 (1958).

[4] R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955), sections IVA and B.

[5] L. Rosenfeld, *Z. Physik*, **52**, 161 (1928).

[6] J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

[7] Clearly the inherently dissymmetric twisted double bond is situated in a molecular environment which is itself dissymmetric. The approximation of the present work is to ignore the weakly perturbing effects of such an environment on the ethylenic chromophore which would in a higher order approximation provide further smaller contributions to the optical activity and also affect the dipole moment (*cf.* ref. (3)).

[8] According to the nomenclature proposed by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), the configuration of IV and V is (*S*) if the double bond is taken as the axially asymmetric frame of reference (as in allenes, biphenyls and the like).

[9] The estimate of ±140° is based in part on the assumption that the twisted six-carbon methylene chain contributes relatively little to the observed rotation at 589 mμ, as might be inferred from the values of $[\phi]_\text{D}$ generally reported for flexible hydrocarbons. Recently P. Pino and G. P. Lorenzi (*J. Am. Chem. Soc.*, **82**, 4745 (1960)) and W. J. Bailey and E. T. Yates (*J. Org. Chem.*, **25**, 1800 (1960)) have shown that certain poly-α-olefins may exhibit enhanced rotations ($[\alpha]_\text{D}$ 200–300°) and the phenomenon has been attributed to stereoregularity in the relevant alkane polymers. Dr. Edel Wasserman points out to us (and we concur in his opinion) that comparable enhancements could conceivably be associated with the more or less rigidly fixed methylene chain in IV and V. In this event, the 10° range of uncertainty for γ would necessarily have to be widened. However, in order that our claims as to absolute configuration be invalidated, the contribution to $[\phi]_\text{D}$ associated with the methylene chain would have to exceed 400°, and this we deem unlikely.

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RECEIVED OCTOBER 10, 1962

ISOMERIZATION AS A PRIMARY PROCESS IN THE PHOTOLYSIS OF CROTONALDEHYDE

Sir:

Previous work on the photolysis of crotonaldehyde has not led to any very definite conclusions about the mechanism of the reaction. Though Blacet and Roof[1] in an early publication stated that no photo-decomposition occurred, later studies[2,3] showed clearly that free radicals were produced and that CO and propylene were the main products. A more recent study[4] of the Hg-photosensitized decomposition of crotonaldehyde confirmed the earlier observations that propylene was a major product and that the reaction produced the propenyl radical. Our recent studies of the photolysis of crotonaldehyde in the gas phase at ∽30° in the wave length range 2450–4000 Å.

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[1] F. E. Blacet and J. G. Roof, *J. Am. Chem. Soc.*, **58**, 73 (1936).

[2] F. E. Blacet and J. E. Lu Valle, *ibid.*, **61**, 273 (1939).

[3] D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

[4] A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **37**, 1696 (1959).

has produced new and novel results which we now report.

Gas chromatographic analysis using several columns of dinonyl phthalate on firebrick showed that after a short period of illumination a peak appeared which was later identified as 3-butene-1-al; somewhat later (*i.e.*, after 3–4 minutes) there appeared chromatographic peaks due to propylene, CO and 1,5-hexadiene. Some polymer also was formed but was not identified.

The identity of the 3-butene-1-al was established by preparing this compound by the oxidation of 3-butene-1-ol with CrO_3 in H_2SO_4 at 2–10°. This procedure was more successful than an attempted Oppenauer oxidation at 130°. Chromatographic analysis of the products of the Oppenauer reaction indicated that crotonaldehyde was the main product. The products from the CrO_3/H_2SO_4 oxidation of 3-butene-1-ol, however, on chromatographic analysis gave a peak at the same place as that found for the "new" product from the photolysis of crotonaldehyde. The infrared spectra of the product thought to be 3-butene-1-al from the photolysis and the compound resulting from the CrO_3/H_2SO_4 oxidation of 3-butene-1-ol were identical. That the oxidation product from 3-butene-1-ol was in fact 3-butene-1-al was confirmed by preparing the 2,4-dinitrophenylhydrazone. After recrystallizing the hydrazone twice from ethanol its m.p. (uncorrected) was found to be 175°, the literature value[5] being 177°.

This observation that 3-butene-1-al is a product of the photolysis of crotonaldehyde shows that an important primary process in this photolytic reaction must be the isomerization reaction

$$CH_3CH{=}CHCHO + h\nu \longrightarrow CH_2{=}CH{-}CH_2{-}CHO \quad (1)$$

The quantum yield for this process is approximately 0.1 and is independent of the concentration of the crotonaldehyde and the light intensity over the range of variation studied. The production of 1,5-hexadiene which we also found is understood easily and its detection provides confirmatory evidence too that the photoisomerization (1) must occur.

The photolysis of 3-butene-1-al would be expected to proceed in the manner shown

$$CH_2{=}CH{-}CH_2{-}CHO + h\nu \longrightarrow CH_2{=}CH{-}CH_2 + HCO \text{ (or } H + CO) \quad (2)$$

and the dimerization of the allyl radical would, of course, lead to the production of 1,5-hexadiene

$$2CH_2{=}CHCH_2\cdot \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 \quad (3)$$

Propylene could be produced from the propenyl radical as indicated by reactions (4), (5a), or (5b)

$$CH_3CH{=}CHCHO + h\nu \longrightarrow CH_3CH{=}CH\cdot + HCO \text{ or } H \pm CO \quad (4)$$

$$CH_3CH{=}CH\cdot + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CH_2 + CH_3CH{=}CHCO \quad (5a)$$

$$CH_3CH{=}CH\cdot + CH_2{=}CHCH_2CHO \longrightarrow CH_3CH{=}CH_2 + CH_2{=}CHCH_2CO \quad (5b)$$

or more likely from the hydrogen abstraction reactions involving the allyl radical as shown in equations (6a) and (6b)

$$\cdot CH_2CH{=}CH_2 + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CH_2 + CH_3CH{=}CHCO \quad (6a)$$

$$\cdot CH_2CH{=}CH_2 + CH_2{=}CHCH_2CHO \longrightarrow CH_3CH{=}CH_2 + CH_2{=}CHCH_2CO \quad (6b)$$

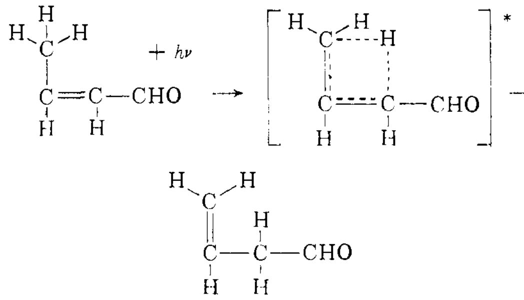
One would expect 1,4-hexadiene to be produced in the photolysis by the recombination reaction (7)

$$CH_2{=}CHCH_2\cdot + CH_3CH{=}CH\cdot \longrightarrow CH_2{=}CHCH_2CH{=}CH_2CH_3 \quad (7)$$

but so far we have not detected this compound. Nor have we been able to detect the presence of 2,4-hexadiene which conceivably could be formed by the recombination of propenyl radicals.

$$2CH_3CH{=}CH\cdot \longrightarrow CH_3CH{=}CHCH{=}CHCH_3 \quad (8)$$

The mechanism of the photoisomerization of crotonaldehyde to 3-butene-1-al is suggested to be[7]



(9)

Acknowledgment.—We wish to thank the National Research Council of Canada for generous grants in support of this work.

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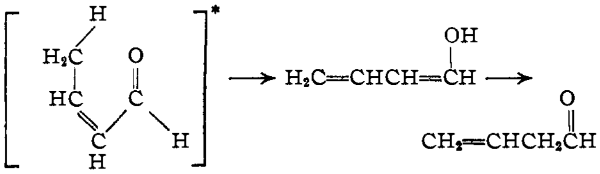
(5) M. F. Shostakovskil, A. V. Bogdanova and G. K. Krasilnikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, 320 (1959); see *Chem. Abs.*, **53**, 19941 (1959).

(6) Holder of a National Research Council Studentship.

(7) A referee has suggested the mechanism



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RECEIVED JULY 23, 1962

NUCLEOPHILIC REACTIVITY OF THE HYDROGEN PEROXIDE ANION: DISTINCTION BETWEEN S_N2 AND S_N1 CB MECHANISMS

Sir:

It already has been shown that the anion of hydrogen peroxide is more reactive than hydroxide ion by factors as large as 10^4 for a number of typical bimolecular nucleophilic displacement (S_N2) reactions.[1,2] These have involved several different substrate molecules but to date no example of a displacement on a simple tetrahedral carbon compound has been studied kinetically. It is known that the reaction

$$RX + O_2H^- \longrightarrow RO_2H + X^- \quad (1)$$

gives hydroperoxide product in a number of cases.[2]

We would like to report the rate of reaction (1) where RX is benzyl bromide. The corresponding

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(1) For a review see J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962); the enhanced reactivity is an example of what has been called the Alpha Effect.

(2) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, pp. 1-11.