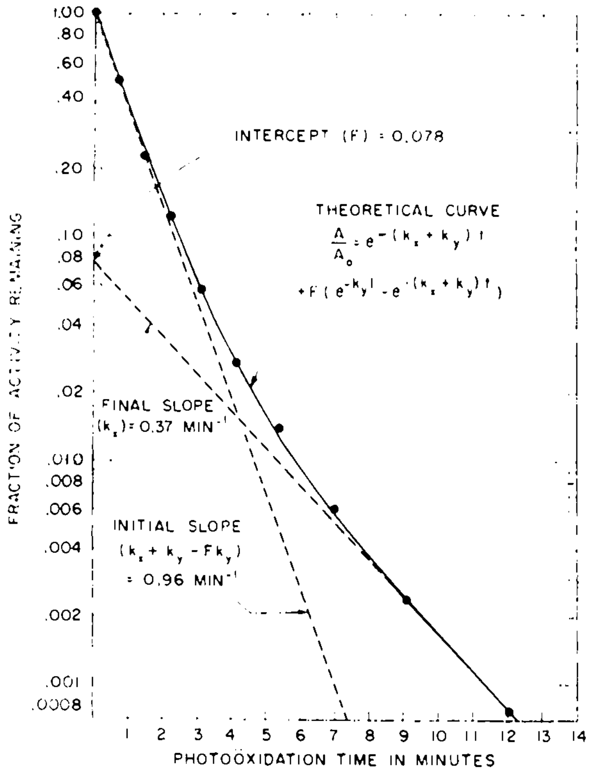

Fig. 2.—Loss of phosphoglucomutase activity on extensive photoöxidation as measured by the "rate" assay.

k_X and k_Y are the rate constants for oxidation of X and Y, and F is the fractional activity in the enzyme modification in which Y has been oxidized. The activity of the enzyme in which X has been oxidized is taken as zero, *i.e.*, undetectable by the present assay procedures. The equation gives a straight line on a semi-log plot only for small values of t in agreement with Fig. 1 but predicts a pronounced curvature at large values of t. When photoöxidation was followed to 99.9% loss of enzyme activity such curvature was found as shown in Fig. 2. Moreover the appropriate graphical analysis led to the evaluation of k_Y, k_X and F as 0.64 min.$^{-1}$, 0.37 min.$^{-1}$ and 0.078, respectively.

To identify the residue, Y, rate constants for oxidation of the various susceptible residues of the enzyme were determined. The first-order rate constant for oxidation of the accessible histidines was found to be 0.65 min.$^{-1}$. As noted previously[1] part of the histidine residues of this enzyme are relatively inaccessible to photoöxidation (k = 0.048 min.$^{-1}$).[2] Since the oxidation constants for other susceptible residues were considerably less than 0.64 (see Ray, *et al.*[3]), it seems quite certain that Y can be identified as an accessible histidine residue.

Both the comparison of the "rate" and "all-or-none" assays and the extension of the rate assay to large values of t lead to the same conclusion, that photoöxidation of a single accessible histidine residue reduces phosphoglucomutase activity by a factor of about 12. Moreover, this concordance suggests that these kinetic methods, which are not theoretically limited to phosphoglucomutase or photoöxidations may be useful in correlating structure with activity in other systems.

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RECEIVED JULY 8, 1960

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[1] D. E. Koshland, Jr., W. J. Ray, Jr., and M. J. Erwin, *Federation Proc.*, **17**, 1145 (1958).

[2] The rate constants are quite dependent on the detailed reaction conditions which will be described in the full publication. In general the photoöxidations were similar to those of Weil, James and Buehert. *Arch. Biochem. Biophys.*, **46**, 266 (1953), except for the use of much higher light intensities.

[3] W. J. Ray, Jr., H. G. Latham, Jr., M. Katsoulis and D. E. Koshland, Jr., THIS JOURNAL, **82**, 4743 (1960).

CONFIGURATION AND OPTICAL ROTATORY DISPERSION OF ATROPISOMERIC BIARYLS[1]

Sir:

Rotatory dispersion curves have been useful in configurational correlations of compounds containing asymmetric atoms.[2] The availability of structurally symmetrical optically active biaryls of known absolute configuration[3] prompted us to secure the rotatory dispersion curves of over sixty compounds in this class. We now report the salient results of our investigation, which lead

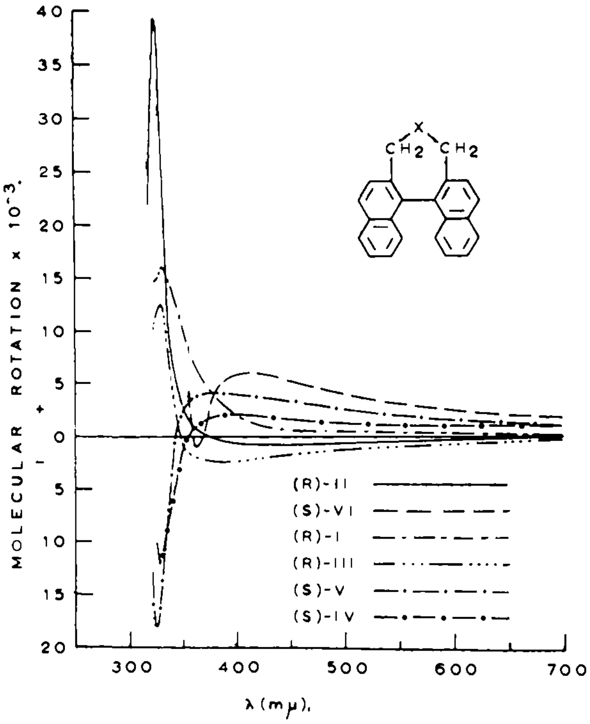

Fig. 1. Optical rotatory dispersion curves (dioxane) of: (R)-I (X = CO); (R)-II (X = $CHOCOCOC_6H_5$); (R)-III (X = CHOH); (S)-IV (X = $C(CO_2C_2H_5)_2$); (S)-V (X = O); (S)-VI (X = direct bond between CH_2 groups).

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[1] Configurational Studies in the Biphenyl Series. IX (paper VIII, K. Mislow and P. A. Grasemann, *J. Org. Chem.*, **23**, 2027 (1958)) and "Optical Rotatory Dispersion Studies. XXXIX" (paper XXXVIII, C. Djerassi, W. D. Ollis and R. C. Russell, *J. Chem. Soc.*, in press).

[2] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, 1960; see especially Chapter 10.

[3] K. Mislow, *Angew. Chem.*, **70**, 683 (1958), and references cited therein.

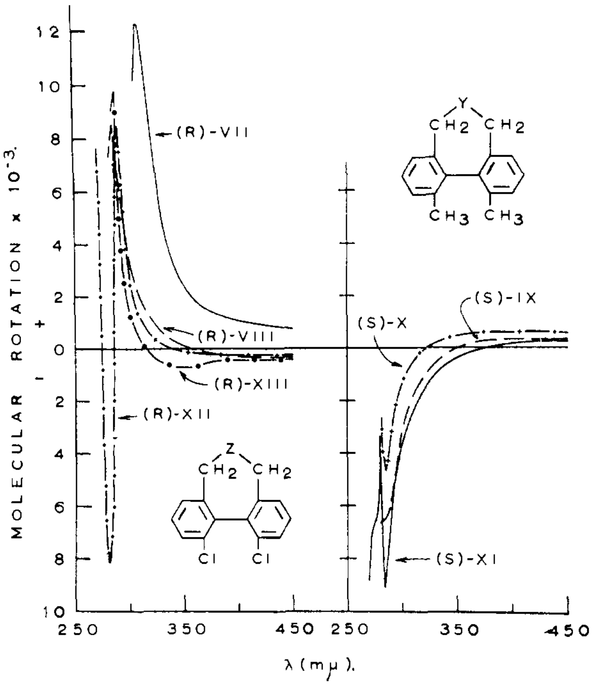

Fig. 2.—Optical rotatory dispersion curves (dioxane) of: (R)-VII) (Y = $C(CO_2C_2H_5)_2$); (R)-VIII (Y = CHOH); (S)-IX (Y = O); (S)-X (Y = CH_2); (S)-XI (Y = CHOH); (R)-XII (Z = $C(CO_2C_2H_5)_2$); (R)-XIII in water (Z = $\overset{+}{N}(CH_2)_5Br^-$).

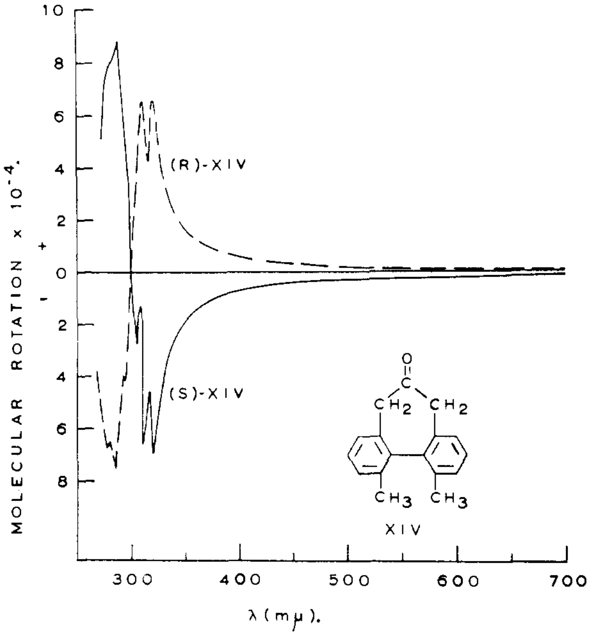

Fig. 3.—Optical rotatory dispersion curves (isoöctane) of (S)-XIV and (R)-XIV.

to the conclusion that *absolute configurations of atropisomers may be successfully correlated by the rotatory dispersion method.*

2,2′-Bridged[4] 1,1′-binaphthyls (Fig. 1) and 2,2′-bridged[4] biphenyls (Fig. 2) of the (R)-configuration exhibit positive Cotton effect curves while negative ones are shown by members of the (S)-series. The visible region is frequently dominated by a background rotation of *opposite* sign (*e.g.*, II or III in Fig. 1). Whenever this is *not* the case (*e.g.*, I in Fig. 1; XIV in Fig. 3) the monochromatic (based on $[\alpha]_D$) bridge rule[5] is violated.[6] The generalization based on rotatory dispersion is therefore more encompassing. Introduction of substituents which profoundly alter the biphenyl chromophore (as in bridged 2,2′-dinitro-, 2,2′-diamino- and 2,2′-dialkoxybiphenyls) drastically changes the rotatory dispersion pattern: thus, bridged (R)-diamino- and dinitrobiphenyls have *negative* rotatory dispersion curves which will be discussed in our detailed paper.

The multiple Cotton effect curves of the bridged ketones (R)-XIV and (S)-XIV (Fig. 3) are distinguished by (i) extraordinary amplitudes and (ii) fine-structure (reflected in the ultraviolet spectrum at $\lambda\lambda_{\max}^{\text{isooct.}}$ 289, 297.5, 307 and 317 mμ) heretofore associated with rotatory dispersion curves of α,β-unsaturated ketones.[2] To account for this observation, we postulate homoconjugation of carbonyl and benzene π-electrons[7]; rotatory dispersion curves may thus serve in the detection of non-contiguous overlaps.[8]

Unbridged 2,2′-substituted 1,1′-binaphthyls behave like the bridged analogs (positive Cotton effect curves for the (R)-configuration). Most unbridged biphenyls appear to follow the same pattern. Unbridged (R)-2,2′-dinitrobiphenyls have *positive* rotatory dispersion curves with λ_0 *ca.* 340 mμ. Comparison of bridged[4] and unbridged biaryl rotatory dispersion curves may yield information on the conformation (*syn-* or *anti-skew*) of the unbridged analogs as will be pointed out in a future paper.

Of the compounds in Figs. 1–3, these have been described previously:[3] (R)-I (X = CO); (R)-II (X = $CHOCOCOC_6H_5$); (R)-III (X = CHOH); (S)-VI (X = direct bond between CH_2 groups); (S)-IX (Y = O); (R)-XIII (Z = $^+N(CH_2)_5Br^-$). These others were prepared from precursors of known[3] absolute configuration: (S)-IV (X = $C(COOEt)_2$), m.p. 163–166° (fd.: C, 79.58; H, 6.04), from (−)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl and malonic ester; (S)-V (X = O), m.p. 152–153° (fd.: C, 89.57; H, 5.53), by dehydration of (−)-2,2′-bis-(hydroxymethyl)-1,1′-binaphthyl; (R)-VII (Y = $C(COOEt)_2$), m.p. 131–132° (fd.: C, 75.34; H, 7.36) from (−)-6,6′-dimethyl-2,2′-bis-(bromomethyl)-biphenyl and malonic ester; (S)-XIV, m.p. 62.5–63.5° (fd.: C, 86.45; H, 6.88), and the enantiomer, (R)-XIV, m.p. 61–63° (fd.: C, 86.26; H, 6.90), by acid hydrolysis of (+)-iminonitrile,[3] respectively, the enantiomer; (S)-XI (Y = CHOH), m.p. 79–81° (fd.: C, 85.55; H,

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[4] Bridging assures a fixed and known (*syn-skew*) conformation.

[5] D. D. Fitts, M. Siegel and K. Mislow, THIS JOURNAL, **80**, 480 (1958).

[6] K. Mislow and F. A. McGinn, *ibid.*, **80**, 6036 (1958).

[7] Suggested by inspection of suitable models (G. Brumlik, Natl. Am. Chem. Soc. Meeting, Cleveland, Ohio, April 13, 1960, Abstracts p. 8-F).

[8] R. C. Cookson and N. S. Wariyar (*J. Chem. Soc.*, 2302 (1959)) have already remarked on the high optical activity which may accompany spectroscopic interaction between a carbonyl group and a β,γ-double bond.

7.53), and the enantiomer, (R)-VIII (Y = CHOH), m.p. 77–79° (fd.: C, 85.94; H, 7.48) by $LiAlH_4$ reduction of (S)-XIV respectively (R)-XIV; (S)-X (Y = CH_2), m.p. 63–64° (fd.: C, 92.05; H, 8.38), by modified Clemmensen reduction of (S)-XIV; (R)-XII (Z = $C(COOEt)_2$), m.p. 165–167° (fd.: C, 61.75; H, 5.07; Cl, 17.29), from (+)-6,6'-dichloro-2,2'-bis-(bromomethyl)-biphenyl and malonic ester.

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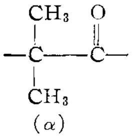
CRYSTALLINE POLYMERS OF DIMETHYLKETENE

Sir:

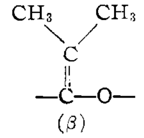
It is known that dimethylketene dimerizes readily to tetramethyl-1,3-cyclobutanedione.[1] Higher polymers were obtained by Staudinger[2] using aliphatic or aromatic amines as catalysts. These amorphous products can be considered as derived from the irregular copolymerization of the two monomeric



$$-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-$$

(α)

and



$$-\overset{CH_3\quad CH_3}{\overset{\diagdown\ \diagup}{\overset{C}{\overset{\|}{C}}}}-O-$$

(β)

units formed, respectively, by the opening of the ethylenic or of the carbonyl double bond.

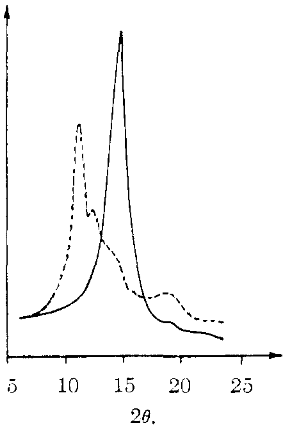


Fig. 1.—X-Ray Geiger registration (CuKα) of the two crystalline poly-dimethylketenes: ——— polymer I, -------- polymer II.

Using ionic catalysts, we have prepared two new types of crystalline dimethylketene polymers of regular chemical structure. Dimethylketene in toluene solution was polymerized at −60° in the presence of aluminum tribromide (moles monomer/moles catalyst approximately 1500); the fraction, which was not extractable with boiling toluene, had an intrinsic viscosity of 0.7 in nitrobenzene at 135°; m.p. 250–255° (determined with a polarizing microscope).

The high crystallinity (see Fig. 1) of this fraction (polymer I) indicates that it is made up of micromolecules having a regular structure. The strong absorption in the infrared spectrum (Fig. 2) near 5.9 μ indicates the presence of carbonyl groups, a conclusion which is confirmed by the ultraviolet spectrum. The two bands around 7.25 μ are in accord with the presence of one type only of gem methyl groups.

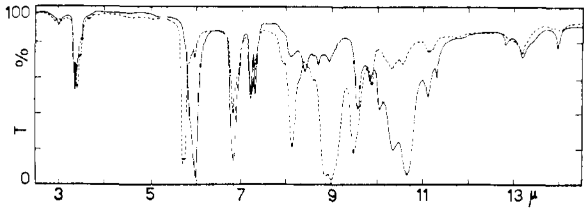


Fig. 2.—Infrared spectra of the two crystalline polydimethylketenes, mulls in Nujol and C_4Cl_6: ——— polymer I, -------- polymer II.

From the chemical properties of polymer I we conclude that it consists of macromolecules formed by the regular head-to-tail enchainment of monomeric units of type (α). In fact, polymer I behaves chemically like a β-diketone; treatment of I suspended in tetrahydrofuran with excess ethyl alcohol and a small quantity of sodium ethoxide, for a long time (100 hours) at 200–260°, yielded ethyl isobutyrate and di-isopropyl ketone in addition to the unchanged polymer.

The structure assigned to polymer I has been confirmed by the results of reduction of the carbonyl groups with $LiAlH_4$. Treatment of I suspended in tetrahydrofuran with $LiAlH_4$ gave a white, amorphous polymer (90% yield) which was insoluble in ether and acetone, but soluble in acetic acid and ethyl alcohol. The infrared spectrum shows that only traces of carbonyl groups remain, whereas there is strong absorption at 3.02 μ which is attributable to associated hydroxyl groups. This reduction product, therefore, is an atactic polymer of polydimethylvinyl alcohol.

Polymerization of dimethylketene under the conditions previously mentioned with triethylaluminum as the catalyst, gave a polymerizate, 70% of which can be extracted with boiling benzene, but not with boiling acetone. This fraction (polymer II) has an intrinsic viscosity of 0.4 (in tetralin at 135°) and a regular structure as indicated by its high crystallinity (see Fig. 1).

The two bands at 5.71 and 5.75μ (only the 5.75μ band occurs in solution) indicate the presence of ester groups. That only traces of carbonyl groups are present is demonstrated by the weak absorption bands at 295 mμ in the ultraviolet.

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(1) H. Staudinger, H. Schneider, P. Schotz and P. M. Strong; *Helv. Chim. Acta*, **6**, 291 (1923).

(2) H. Staudinger, *ibid.*, **8**, 306 (1925).