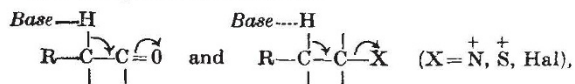


The comparison is between



the former diagram representing the rate-determining step of a base-catalysed enolization, the latter an ordinary elimination by mechanism *E2*. The difference is that the combination CO does not break up completely while CX does. The question to be considered is whether the effect of alkyl groups R on the rate of enolization of a ketone (now regarded as an elimination reaction) will be of the 'Hofmann type' or the 'Saytzeff type'. Relatively to CX, the stretching of CO in the transition state must be small, and accordingly the electron defect on the carbon atom and the dependent quasi-conjugation, developed in the course of reaction, may be assumed to be comparatively unimportant. It is therefore not surprising that the effect of alkyl groups on rate is found to be of the Hofmann type. This may be illustrated by Evans and Gordon's results<sup>2</sup> for the rate of bromination (kinetically equivalent to enolization) of phenyl alkyl ketones, CHR'R'.CO.Ph in the presence of acetate ions as basic catalyst:

R, R'	H, H	Me, H	Et, H	Pr <sup>β</sup> , H	Me, Me
10 <sup>3</sup> k <sub>45</sub> <sup>o</sup>	52.0	7.99	6.24	3.05	1.55

Examples of 'Hofmann influences' are also to be found in the effect of alkyl substitution on rate of interconversion in the case of 'three-carbon' prototropy.

A contrast to these effects on reaction rate is afforded by evidence that the effects of alkyl substituents on prototropic equilibria are essentially dependent on the same internal mechanism as underlies what have here been called Saytzeff influences on rate (preceding note). The ground states alone are important for equilibria, with the result that, in the tautomerism of olefinic acids, for example, the introduction of a γ-alkyl group shifts the equilibrium in favour of the βγ-form. Consistently a methyl group is more effective in this respect than higher alkyl groups. This effect may be illustrated by the results of Kon and Linstead<sup>3</sup> for the base-catalysed equilibria of the anions of a series of acrylic acids, RR'C=CH.CO<sub>2</sub>H:

RR'	Me <sub>2</sub>	Et <sub>2</sub>	Pr <sup>α</sup>	iso-Bu <sub>2</sub>
γ-substituent	H	CH <sub>3</sub>	.CH <sub>2</sub> CH <sub>3</sub>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH} \\   \\ \text{CH}_3 \end{array}$
αβ-form (%)	100	5	33	49

The importance of quasi-conjugation for equilibria may also be illustrated with reference to anionotropic change. The predominating formation of crotyl and cinnamyl halides in the equilibration of the butenyl and phenylpropenyl halides are familiar examples.

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<sup>1</sup> Ingold, E. H., *Chem. and Ind.*, 42, 1246 (1923); *J. Chem. Soc.*, 123, 1717 (1923).

<sup>2</sup> *J. Chem. Soc.*, 1434 (1938).

<sup>3</sup> Cf. Kon and May, *J. Chem. Soc.*, 1549 (1927); Ingold, *Ann. Rep. Chem. Soc.*, 24, 112 (1927).

## FORTHCOMING EVENTS

Friday, July 4

GEOLOGISTS' ASSOCIATION (at the Geological Society of London, Burlington House, Piccadilly, London, W.1), at 5.30 p.m.—Dr. A. J. Bull: Opening Paper of a Discussion on "Pleistocene Chronology".

## APPOINTMENTS VACANT

APPLICATIONS are invited for the following appointments on or before the dates mentioned:

LECTURER IN MATHEMATICS—The Secretary, Technical College, Sunderland (July 5).

LECTURER IN THE DEPARTMENT OF MINING—The Registrar, University, Leeds (July 7).

LECTURER FOR THE (CIVIL AND MECHANICAL ENGINEERING DEPARTMENT)—The Secretary, Northampton Polytechnic, St. John Street, London, E.C.1 (July 7).

## REPORTS AND OTHER PUBLICATIONS

(not included in the monthly Books Supplement)

### Great Britain and Ireland

Empire Cotton Growing Corporation. Annual Report for the Season 1939-1940. Pp. ii+34. (London: Empire Cotton Growing Corporation.) [295]

Institute of Physics. Twenty-first Annual Report of the Board, 1940. Pp. 16. (Reading: Institute of Physics, c/o The University.) [66]

Eating for Victory: Suggestions for War-time Economy in Food-stuffs. A Sequel to "Grass for All". By J. R. B. Branson. Pp. 20. (Bordon, Hants.: Branson's Publications.) 4d. [66]

Annual Report of the Zoological Society of Scotland for the Year ending 31st March 1941. Pp. 28. (Edinburgh: Zoological Society of Scotland.) [96]

Carnegie United Kingdom Trust. Twenty-seventh Annual Report, 1940. Pp. vi+46+2 plates. (Dunfermline: Carnegie United Kingdom Trust.) [96]

Institution of Gas Engineers. Communication No. 240: The Gas Industry, 1941 and After: a Symposium. Pp. 60. (London: Institution of Gas Engineers.) [96]

### Other Countries

Herbertia. Vol. 7. Dedicated to Latin America. Edited by Hamilton P. Traub. Pp. 242. (Orlando, Fla.: American Amaryllis Society.) 3.25 dollars. [285]

United States Department of Agriculture: Weather Bureau. Monthly Weather Review, Supplement No. 46: Observations of Nocturnal Radiation at Fairbanks, Alaska, and Fargo, N. Dak. Pp. ii+22. (Washington, D.C.: Government Printing Office.) 10 cents. [285]

Field Museum of Natural History. Botanical Series, Vol. 9, No. 6: Studies of the Vegetation of Missouri, 2: Phanerogamic Flora of the Fresh-Water Springs in the Ozarks of Missouri. By Julian A. Steyermark. (Publication 491.) Pp. 477-618+24 plates. 1.25 dollars. Zoological Series, Vol. 22, No. 7: New and Little Known Neotropical Histeridae (Coleoptera). By Rupert L. Wenzel and Henry S. Dybas. (Publication 492.) Pp. 431-472+plates 13-16. 40 cents. Zoological Series, Vol. 24, No. 19: Birds from the Yucatan Peninsula. By Melvin A. Taylor, Jr. (Publication 493.) Pp. 195-226. 20 cents. (Chicago: Field Museum of Natural History.) [285]

Geological Survey of British Guiana. Bulletin No. 15: Report on the Geology and Mineral Deposits of the Upper Waini River, North West District. By Dr. D. A. Bryn Davies. Pp. iii+22. (Georgetown: Geological Survey.) 24 cents. [46]

Indian Forest Records (New Series). Botany, Vol. 1, No. 7: Contributions to our Knowledge of the Morphology, Cytology and Biology of Indian Coniferous Rusts. Part 1: *Cronartium himalayense* Bagchee and *Peridermium orientale* Cooke on *Pinus longifolia* Roxb. By K. Bagchee. Pp. iii+247-266. (Delhi: Manager of Publications.) 1.6 rupees; 2s. [66]

Recent Developments in the Science of Plant and Animal Nutrition and their Significance to National Nutrition and Health. Presidential Address to the Section of Chemistry and Biology, 10th Annual Meeting of the National Academy of Sciences, February 1941, by Rao Bahadur B. Viswa Nath. Pp. 31+iii. (New Delhi: The Author, Imperial Agricultural Research Institute.) [66]

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