

We wish now to report the synthesis of N^6 - β -glyceryl-D,L-lysine and the results of comparison of this synthetic substance with the radioactive amino acid obtained on acid hydrolysis of the sodium borohydride-reduced complex from the C^{14} -fructose 6-phosphate-transaldolase reaction.

Reaction of 5- δ -bromobutylhydantoin with a tenfold excess of 2-amino-1,3-propanediol for 37 hr. in boiling, absolute ethanol gave 5- δ -(β -glyceryl)-butylhydantoin; this product was separated from unchanged 2-amino-1,3-propanediol on the hydroxide form of Amberlite IRA-400 (Rohm and Haas Co.) and isolated in the form of a heavy sirup by eluting the resin with 1 *M* acetic acid and evaporating this eluate at reduced pressure. Hydrolysis of the crude 5- δ -(β -glyceryl)-butylhydantoin in 2 *M* sodium hydroxide for 17 hr. at 100° under nitrogen gave the N^6 - β -glyceryl-D,L-lysine from which any unhydrolyzed hydantoin was removed by acidifying the mixture to pH 5 and equilibrating it with the hydroxide form of Amberlite IRA-400. After desalting the resulting solution on Amberlite CG-120 by the method of Dreze, *et al.*,⁵ N^6 - β -glyceryl-D,L-lysine dihydrochloride was isolated as an exceedingly hygroscopic glass by evaporating the portion of the 4 *M* hydrochloric acid eluate in which it appeared in the desalting operation and drying the residue over barium oxide. Equilibration of an aqueous solution of this dihydrochloride with the hydroxide form of Amberlite IRA-400, followed by elution of the resin with 1 *M* acetic acid and vacuum evaporation of the eluate, gave N^6 - β -glyceryl-D,L-lysine free base in the form of a heavy sirup. Adding ethyl ether to an absolute ethanol solution of this product precipitated it as a colorless solid, m.p. 155–57° (with decomposition). *Anal.* Calcd. for $\text{C}_9\text{H}_{20}\text{N}_2\text{O}_4$: C, 49.07; H, 9.11; N, 12.72. Found: C, 48.66; H, 8.97; N, 12.41; ash, 0.61.⁶

As shown in Fig. 1, the migration of synthetic N^6 - β -glyceryl-D,L-lysine during electrophoresis was identical with that of the radioactive amino acid obtained from the C^{14} -fructose 6-phosphate-transaldolase complex; further, synthetic N^6 - β -glyceryl-D,L-lysine underwent complete conversion to lysine under the same conditions of periodate treatment that oxidized the radioactive amino acid to lysine. These data provide final proof for the structure of the radioactive amino acid obtained in the experiments with aldolase and transaldolase; thus, these findings are completely in accord

(5) A. Dreze, S. Moore, and E. J. Bigwood, *Anal. Chim. Acta*, **11**, 554 (1954).

(6) Microanalysis by Spang Microanalytical Laboratory, Ann Arbor, Mich.

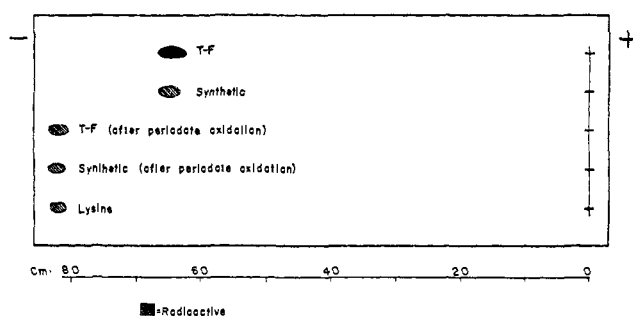


Fig. 1.—Electrophoresis pattern of the radioactive amino acid (T-F) (from the transaldolase-fructose 6-phosphate system) and synthetic N^6 - β -glyceryl-D,L-lysine (synthetic) before and after periodate oxidation. Electrophoresis was carried out in 4% acetic acid, 4% formic acid (pH 1.8) at 5000 v. and at 20–30° for 2 hr. The quantities of synthetic N^6 - β -glyceryllysine and T-F used for electrophoresis were 3×10^{-8} and approximately 5×10^{-9} mole, respectively. The periodate-oxidized samples were equivalent to 1×10^{-8} mole of the synthetic amino acid and approximately 4×10^{-9} mole of T-F; 1×10^{-8} mole of lysine was used for reference.

with the concept of Schiff base intermediates in these reactions and with an earlier hypothesis of operation of immonium ion catalysis (specific amine catalysis) in aldolase-catalyzed reactions.⁷

(7) J. C. Speck, Jr., and A. A. Forist, *J. Am. Chem. Soc.*, **79**, 4459 (1957).
(8) Given Foundation-National Research Fellow in Academic Medicine.

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EVIDENCE FOR THE EXISTENCE OF GROUP VI METAL PENTACARBONYLS

Sir:

In a recent communication¹ we presented evidence for the photoproduction of $\text{W}(\text{CO})_5$, which is believed^{2–4} to be an intermediate in the formation of tungsten carbonyl derivatives through the replacement of one or

(1) I. W. Stolz, G. R. Dobson and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962).

(2) L. E. Orgel, *Nature*, **191**, 1387 (1961).

(3) G. R. Dobson, M. A. ElSayed, I. W. Stolz and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962).

(4) W. Strohmeier, *Chem. Ber.*, **94**, 3337 (1961).

TABLE I
CARBONYL STRETCHING FREQUENCIES FOR SOME LOWER METAL CARBONYLS

Normal carbonyl	Observed frequencies upon irradiation in 1:4 isopentane-methylcyclohexane glass	Assignments
W(CO) ₆	2092 (w), 1952 (s), 1924 (m)	as W(CO) ₆ , C _{4v} symmetry
Mo(CO) ₆	2093 (w), 1960 (s), 1922 (m)	as Mo(CO) ₆ , C _{4v} symmetry
Mo(CO) ₆	2007 (s), 1995 (s)	as Mo(CO) ₆ , D _{3h} symmetry
Cr(CO) ₆	2088 (w), 1955 (s), 1928 (m)	as Cr(CO) ₆ , C _{4v} symmetry
Fe(CO) ₅	1990 (s), 1980 (w), 1946 (s)	

Band intensities: w = weak, m = medium, s = strong.

more CO groups by ligands such as ethers, nitriles and olefins. Further work, utilizing improved equipment, has led to significant information concerning a transition between structures for such species. We also have obtained evidence for the photoproduction of two new species, Mo(CO)₅ and Cr(CO)₅.

Carefully purified 1:4 isopentane-methylcyclohexane solutions 0.01 M in the normal hexacarbonyl (Cr(CO)₆, Mo(CO)₆ or W(CO)₆) were cooled under an inert atmosphere with liquid nitrogen in an infrared cold cell with NaCl windows. Through use of this cell it was possible to irradiate the metal carbonyl-containing glasses and to record their spectra for the carbonyl-stretching region of the infrared (2200-1700 cm.⁻¹) at -180°. The cell temperature was measured through use of an iron-constantan thermocouple. The spectrum of the irradiated Mo(CO)₆ glass was also recorded as the glass was slowly warmed to the fluid state. Results are shown in Table I.

The spectra obtained in frozen glasses for the carbonyl-stretching region of the infrared for these group VI lower carbonyls are consistent as to number, position and intensity of bands to those predicted by group theoretical considerations for pentacoordination of C_{4v} symmetry.⁵ The bands observed for W(CO)₆ were at slightly higher frequencies than were those reported in the earlier communication.¹

We have been able to discount the possibility that these lower carbonyl complexes may actually involve the replacement of a carbonyl group by a dissolved gas or solvent molecule. A sample of W(CO)₆ was sublimed under high vacuum onto a cold-finger and was exposed to ultraviolet radiation at -196°. A yellow-brown product was produced. After the irradiation was stopped, this product was treated *in vacuo* with acetonitrile to yield W(CO)₅(CH₃CN).

As the glass containing Mo(CO)₆ was warmed to the fluid state there occurred a rapid conversion from the three carbonyl bands characteristic of the square pyramidal carbonyl configuration to two bands of approximately equal intensity (Table I). The glass softens at between -165° and -160°, while this transition occurs at about -155°. The latter spectrum is consistent with D_{3h} symmetry and is quite similar⁶ to that of Fe(CO)₅, which has been proven⁷ to be trigonal bipyramidal. We suppose that in the glass the Mo(CO)₆ molecule is unable to assume the more expected trigonal bipyramidal configuration. Evidence for the restriction of molecular motion in the glass which could enable the Mo(CO)₆ molecule to retain C_{4v} symmetry in preference to D_{3h} comes from the similarity of position and shape between the stretching band due to trapped CO in our work and that reported by Ball⁸ for clathrate complexes in which the presence of the CO Q branch indicates that the CO molecules are unable to rotate freely in the cage. For these clathrate complexes the

CO band is reported at 2133 cm.⁻¹, while we observe the free CO stretch at 2135 cm.⁻¹. These characteristic CO stretching bands are observed for each lower carbonyl produced, and disappear as the carbonyl reverts substantially (about 70%) to its parent.

We also have observed, in similar experiments with Fe(CO)₅, three bands (Table I) which we believe to be the carbonyl stretching frequencies of an intermediate iron carbonyl species. Work on this aspect of the problem is continuing.

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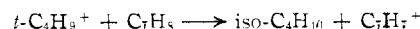
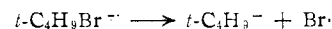
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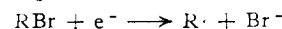
A RADIATION-INDUCED PREPARATION OF TROPYLIUM BROMIDE¹

Sir:

Our interest in the significance of ionic reactions in radiation chemistry led us to explore a direct radiation-induced route to the formation of the ionic salt, tropylium bromide. One of the most useful preparative methods involves the primary generation of a carbonium ion which subsequently reacts with cycloheptatriene by hydride ion transfer. Thus triphenylmethyl bromide and cycloheptatriene react in a strong ionizing solvent such as liquid sulfur dioxide,² and Friedel-Crafts catalysts are also known to promote the formation of the tropylium ion by a similar mechanism.³ We reasoned that if ionizing radiation produces the *t*-butyl carbonium ion from the fragmentation of the *t*-butyl bromide parent ion,⁴ a way would then be open for the preparation of tropylium bromide without the agency of ionizing solvent or added catalyst; this prospect seemed



all the more inviting in view of recurring evidence⁵ that alkyl bromides undergo dissociative electron capture, even in the liquid state.



As envisaged, a tropylium cation and a bromide anion would be formed upon the radiolysis of *t*-butyl bromide containing cycloheptatriene; it is the purpose of this Communication to report that tropylium bromide is indeed produced under these conditions.

(1) This research is supported by A.E.C. Contract No. AT-(40-1)-2968.

(2) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(3) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961), and references therein.

(4) Our initial choice of *t*-butyl bromide was dictated by the ease of formation of branched carbonium ions from the dissociation of excited parent molecule-ions as revealed by mass spectra. This point, and its relevance to liquid phase studies, is discussed in some detail elsewhere; cf. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961), and *Quart. Rev.*, in press.

(5) W. Van Dusen, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962), and references therein.

(5) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(6) The CO stretching frequencies for Fe(CO)₅ are found at 2023 (s) and 1917 (s) cm.⁻¹.

(7) A. W. Hanson, *Acta Cryst.*, **15**, 930 (1962).

(8) D. F. Ball and D. C. McKean, *Spectrochim. Acta*, **18**, 933 (1962).