6.0; N, 7.3; $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 265, 350 mμ, log ε 4.34, 4.21, $[\alpha]^{25}\mathrm{D} -191°$, R_f 0.02), 9-amino-6-demethyl-6-deoxytetracycline (XII, found for $C_{21}H_{23}N_3O_7 \cdot 1.5H_2O$: C, 54.8; H, 5.8; N, 8.9; $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 265, 350 mμ, log ε 4.33, 4.25, $[\alpha]^{25}\mathrm{D} -212°$, R_f 0.02), and 9-amino-6-deoxytetracycline (XIII, found for $C_{22}H_{25}N_3O_7 \cdot C_4H_9OH \cdot 2H_2SO_4$: C, 43.7; H, 5.4; N, 6.2; $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 265, 350 mμ, log ε 4.26, 4.17, $[\alpha]^{25}\mathrm{D} - 211°$, R_f 0.02).

Bromination and nitration of 9-amino-6-deoxytetracycline under the previously described conditions yielded 9-amino-7-bromo-6-deoxytetracycline (XIV, found for $C_{22}H_{24}N_3O_7Br \cdot H_2O \cdot 2H_2SO_4$: C, 36.0; H, 4.5; N, 10.9; $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 265, 348 mμ, log ε 4.31, 4.07, $[\alpha]^{25}\mathrm{D} -153°$, R_f 0.44) and 9-amino-7-nitro-6-deoxytetracycline (XV, found for $C_{22}H_{24}N_4O_9 \cdot 2H_2SO_4$: C, 38.8; H, 4.7; N, 8.0; $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 261, 348 mμ, log ε 4.32, 414, $[\alpha]^{25}\mathrm{D} -300°$, R_f 0.48), respectively. The position of the bromo and nitro groups in the aromatic ring was proved by the use of tritium labeled starting material.

The relative *in vitro* antibacterial activities of the compounds described in this paper are presented in Table I.

TABLE I

In Vitro ANTIBACTERIAL ACTIVITY IN % COMPARED TO 7-CHLOROTETRACYCLINE[a]

6-Deoxytetracycline (I)	18
6-Demethyl-6-deoxytetracycline (II)	40
7-Bromo-6-demethyl-6-deoxytetracycline (III)	60
7-Iodo-6-demethyl-6-deoxytetracycline (IV)	30
7-Bromo-6-deoxytetracycline (V)	30
7-Iodo-6-deoxytetracycline (VI)	14
7-Nitro-6-demethyl-6-deoxytetracycline (VII)	160
9-Nitro-6-demethyl-6-deoxytetracycline (VIII)	3
7-Nitro-6-deoxytetracycline (IX)	60[8]
9-Nitro-6-deoxytetracycline (X)	<1
7-Amino-6-demethyl-6-deoxytetracycline (XI)	21
9-Amino-6-demethyl-6-deoxytetracycline (XII)	40
9-Amino-6-deoxytetracycline (XIII)	14
9-Amino-7-bromo-6-deoxytetracycline (XIV)	35
9-Amino-7-nitro-6-deoxytetracycline (XV)	41

[a] Activities were measured turbidimetrically against *Staph. aureus* by the method of E. Pelcak and A. Dornbush, *Ann. N. Y. Acad. Sci.*, **51**, 218 (1948).

Acknowledgment.—The authors wish to thank Mr. L. Brancone and associates for the microanalyses, Mr. A. Dornbush and associates for antibacterial assays, Miss R. Livant for paper chromatography results, Mr. W. Fulmor and co-workers for the spectral data, and Dr. D. Buyske for radiometric analysis of tritiated compounds.

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RECEIVED JANUARY 25, 1960

THE INFRARED SPECTRA OF METAL CARBONYLATE IONS. BONDING CONSIDERATIONS

Sir:

The infrared spectra of various solid salts of $Co(CO)_4^-$, $Fe(CO)_4^{=}$ and $HFe(CO)_4^-$, of water solutions of these ions in the 5μ region, and of tetrahydrofuran and diglyme solutions of $Mn(CO)_5^-$ and $Co(CO)_4^-$ have been examined with prisms and small gratings. Averages of components split by crystal effects are given when only data on solids are available. The results are $Co(CO)_4^-$: 1886(vs), 555(s), 530(w); $Fe(CO)_4^{=}$: 1786(vs), 646(s), 556(m); $HFe(CO)_4^-$: 2015 (w), 1937(sh), 1897(vs), 693(m), 618(s), 594(m), 540(w), 513(?); $Mn(CO)_5^-$: 1898(vs), 1863(vs) 683(s), 659(s), 564(w), 511(m), 467(m) cm.$^{-1}$. The two stronger bands of $Co(CO)_4^-$ previously were reported by Friedel, *et al.*,[1] while those for $Fe(CO)_4^{=}$ and $HFe(CO)_4^-$ correspond, with several exceptions, to Raman lines recently found by Stammreich and co-workers.[2]

The C–O stretching frequencies in isoelectronic, isosteric series have significance in relation to a simplified molecular orbital model of the bonding.[3] Following the lead of Edgell and Gallup,[4] the "lone-pair" σ_{CO}, the π_{CO} and the π^*_{CO} orbitals of carbon monoxide and the 3d, 4s, and 4p orbitals of the metal are considered as starting orbitals. Consider the case of the $M(CO)_4$ species. Using symmetry and rough energy arguments, the lower energy or "B orbitals" of the molecular species consist of nine bonding orbitals plus three, nonbonding, π_{CO} orbitals. The five remaining occupied or "A orbitals" may be thought of as closing an electron shell. When the relative energies of the π^*_{CO} orbitals are so high that they make no contribution to the A subshell orbitals, the latter will be antibonding between the metal and the CO groups. But with energy decrease, the addition of π^*_{CO} character to the A orbitals may be expected to result in energy stabilization of this subshell, a reduction in metal-CO antibonding character, and the appearance of C–O antibonding character. Thus, the π^*_{CO} character of the A orbitals is an important factor in the bonding description.

The C–O stretching frequencies in $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{=}$ are 2057, 1886 and 1786 cm.$^{-1}$, respectively; the values at 1898 and 1863 for $Mn(CO)_5^-$ correspond to 2034 and 2014 for $Fe(CO)_5$, while 1897, 1937 for $HFe(CO)_4^-$ are shifted from 2043, 2062 cm.$^{-1}$ for $HCo(CO)_4$. These large frequency decreases with anionic charge result from increasing π^*_{CO} character of the A orbitals. It may be estimated that the *drop* in the C–O force constant factor, $k_{\mathrm{CO}} - k_{\mathrm{CO,CO}}$, is about 4.4 md./A. in going from $Ni(CO)_4$ to $Fe(CO)_4^{=}$. This corresponds to a *substantial* increase in π^*_{CO} stabilization and suggests that the order of the Ni–C bond may not be as large as sometimes estimated.

These results imply that the C–O stretching frequencies are an important diagnostic for bonding character in similar molecules. These considerations have been applied to such molecules as $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Fe(CO)_4I_2$, $HgFe(CO)_4$, the hydrides, *etc.*

The spectra of $Fe(CO)_4^{=}$ and $Co(CO)_4^-$ are consistent with tetrahedral structures; that of Mn-

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(1) R. Friedel, I. Wender, S. Shufler and H. Sternberg, THIS JOURNAL, **77**, 3951 (1955).

(2) H. Stammreich and co-workers, private communication.

(3) W. F. Edgell, Abstracts, 134th Meeting Am. Chem. Soc., Chicago, Ill., Sept., 1958; talks before various A.C.S. local sections 1958–1959.

(4) W. F. Edgell and G. Gallup, THIS JOURNAL, **78**, 4188 (1956).

$(CO)_5^-$ resembles the spectrum of $Fe(CO)_5$ and might indicate a similar structure. The spectrum of $HFe(CO)_4^-$ correlates nicely with those of $Fe(CO)_4^=$ and $H_2Fe(CO)_4$. The decrease in molecular symmetry with addition of hydrogen is clearly evident.

Professor J. Richardson is thanked for helpful discussions on orbital theory.

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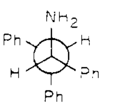
RECEIVED DECEMBER 18, 1959

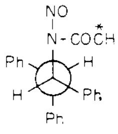
A RADIOCHEMICAL CRITFRION FOR CONFIGURATIONAL RELATIONSHIP

Sir:

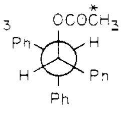
It has been shown[1] that N-nitrosoamides undergo thermal decomposition in polar and in non-polar solvents with net retention of configuration. To our knowledge, however, such decompositions have not yet been used as criteria for configurational relationships. In connection with studies of the stereochemical course of the deamination of 1,2,2-triphenylethylamine (I), it became necessary to relate the configuration of (+)-I with that of (+)-1,2,2-triphenylethanol[(+)-IV].[2] In order that the N-nitrosoamide decomposition could be used for this purpose, additional verification of its stereochemical course in the decomposition of (−)-N-acetyl-N-nitroso-1,2,2-triphenylethylamine [(−)-II] was necessary. In combination with appropriate tracer studies, such verification now has been obtained. Thus, D-(−)-II, labeled with carbon-14 in the acetyl group, was prepared from D-(+)-I, and thermally decomposed in purified acetic acid at 40.5°. The product, consisting of 70% (+)-III and 30% (−)-III, was fractionally crystallized and each fraction [(+) and (±)] was assayed for carbon-14. It was shown that (+)-III contained 29.2% of the carbon-14 originally in D-(−)-II, whereas (−)-III contained only 3.3% of the original radioactivity. In a repetition of this experiment with D-(+)-II, (−)-III contained 29.5% and (+)-III 3.7% of the original carbon-14. Since the labeled acetate group in II should be expected to remain preferentially in the same configuration during the decomposition to III, whereas solvent acetate should attack preferentially with inversion, the D-configuration now can be assigned without hesitation to (+)-I, (−)-II, (+)-III and (+)-IV.[3,4]



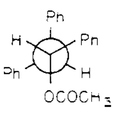
D-(+)-I



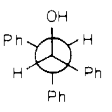
D-(−)-II



D-(+)-III



L-(−)-III



D-(+)-IV

In a typical experiment, 3.0 g. of D-(+)-N-acetyl-C^{14}-1,2,2-triphenylethylamine,[4] $[\alpha]^{25}_{D}$ 109° (dioxane) (molar radioactivity, 7.941 mc. carbon-14) was converted to 3.15 g. of D-(−)-II, $[\Delta]^{25}_{D}$ −320° (benzene), by the method of France, Heilbron and Hey.[5] The material could not be obtained free from contaminating amide, as efforts to crystallize the sample resulted in its decomposition. Carbon and hydrogen determinations gave variable, unsatisfactory results. The purest sample obtained exhibited a molecular weight of 343.8 ± 1.3 (calcd. 344.4), as determined by radioactivity assay. A solution of 2.12 g. of D-(−)-II in 200 ml. of acetic acid was kept at 40.5° until reaction was complete, as shown by optical rotation of the solution. Samples of (+)-III and (±)-III were obtained by fractional crystallization of the product from 95% ethanol, and their purity was checked by infrared analyses. The sample of (+)-III showed on radioactivity assay 3.353 mc. carbon-14 per mole, whereas the (±)-III showed on radioactivity assay 2.168 mc. per mole, allowing the calculation that (−)-III contained 0.982 mc. of carbon-14 per mole.[6,7,8]

Acknowledgment.—The authors wish to acknowledge the encouragement and support given J. B. C. by the late Professor Cash B. Pollard of the University of Florida.

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[1] (a) R. Huisgen and H. Nakaten, *Ann.*, **586**, 84 (1954); R. Huisgen and Ch. Rüchardt, *ibid.*, **601**, 21 (1956); (b) E. H. White, THIS JOURNAL, **76**, 4497 (1954); **77**, 6008, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **80**, 2597 (1958).

[2] C. J. Collins, W. A. Bonner and C. T. Lester, *ibid.*, **81**, 466 (1959).

[3] (+)-1,2,2-Triphenylethyl acetate (III) has been converted to (+)-1,1,2-triphenylethylene glycol by treatment with N-bromosuccinimide and alkaline hydrolysis [C. J. Collins, unpublished work]. The (+)-glycol is obtainable from D-(−)-mandelic acid by treatment with phenylmagnesium bromide [A. McKenzie and H. Wren, *J. Chem. Soc.*, **97**, 473 (1910)], and the absolute configuration of mandelic acid has been established by Mislow [K. Mislow, THIS JOURNAL, **73**, 3954 (1951)].

[4] D-(+)-III yields D-(+)-IV upon treatment with lithium aluminum hydride.[2]

[5] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

[6] A detailed study of the stereochemistry and radiochemistry of the thermal decomposition of D- and L-II will be reported at a later date. Since chain-labeling experiments similar to those previously[2] reported indicate phenyl migration during the decomposition of II, the rather considerable amount of labeled acetoxyl associated with D-(−)-III may be attributed to inversion arising through phenyl migration through a *cis*-transition state in the ionic intermediates involved.

[7] Taken from the Ph.D. dissertation of Dr. Joan B. Christie, University of Florida, Gainesville, August, 1959. Predoctoral Fellow of the Oak Ridge Institute of Nuclear Studies.

[8] This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission.

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RECEIVED JANUARY 18, 1960

THE ENERGY DIFFERENCE BETWEEN THE BOAT AND CHAIR FORMS OF CYCLOHEXANE

Sir:

It is well accepted that the chair is more stable than the boat form of cyclohexane; however, attempts to estimate the magnitude of this energy difference have yielded values ranging from as little as 1.31[1] to as much as 10.6[2] kcal./mole. We re-

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[1] The lower value of the range calculated by D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).

[2] The higher value of a range calculated by the Turner semi-empirical method as described by W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 15.