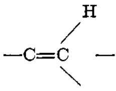
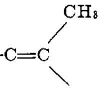
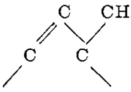
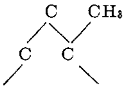
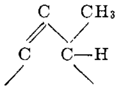
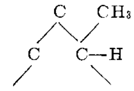
TABLE II

SOME PERTINENT N.M.R. DATA OF THE CYCLOOLEFINS

	Purity[c]	Im-purity	Chemical shifts (c.p.s.)[a]				Spin–spin splittings[b]	
								
(+)-2,4-Dimethylcyclohexene	90.6	1,3-	314[d]	91	..	51	..	5.4
(+)-1,3-Dimethylcyclohexene	91.8	2,4-	308[d]	92	52	..	7.0	...
(−)-3-Methylmethylenecyclohexane	98.4	1,3-	268[e]	..	..	48	...	5.4

[a] Spectra obtained on scale of 500 c.p.s.; external standard of tetramethylsilane; error is about ±2 c.p.s. [b] Spectra obtained on scale of 100 c.p.s.; error is ±0.2 c.p.s.—this is X-part of typical AX_3 type system, A-part is buried in envelope caused by protons attached to ring. [c] Purer fractions were not of sufficient volume for obtaining n.m.r. data. [d] Integrated areas show one proton. [e] Integrated areas show two protons.

(−)-3-methylmethylenecyclohexane. This fact coupled with different splitting of the 50-c.p.s. peaks of (+)-2,4-dimethylcyclohexene and (+)-1,3-dimethylcyclohexene establishes the relative structures; *i.e.*, the 2,4-olefin has one methyl similar to the one on the *exo*-olefin but the 1,3-olefin does not.

There is a more fundamental means of deciding which spectra represents the 1,3- and which represents the 2,4-olefin other than merely comparing the spectra with that of the *exo*-olefin. The methyl doublets around 50 c.p.s. appear at first glance to be B-parts of typical AB_3 spectra; however, the difference in chemical shifts (δ) between the tertiary proton and the methyl group is large enough in each case (*i.e.*, $J/\delta < 0.25$) to be considered AX_3 systems, and both methyl groups should be sharp doublets.[6,7] This is the case for the 1,3-olefin, but for the 2,4-olefin the doublet is not so well resolved and a shoulder is present on the upfield side of the less intense member. Therefore, these splitting patterns should be interpreted along the lines suggested by Anet[8] to explain the splittings of the methyl groups of certain 6α- and 6β-methyl steroids. The tertiary proton is coupled to protons on carbons adjacent to it in the ring and, even though these adjacent protons do not split the methyl protons, they influence the splitting between the tertiary proton and the methyl protons. This secondary effect is minimized when the ratio J/δ between the tertiary proton and adjacent ring protons becomes less than 0.5.[8] Our data are in agreement with this explanation, for when the tertiary proton is allylic and shifted away from the ring protons as in the 1,3-olefin, the methyl group doublet at 50 c.p.s. is split to the base line. However, when the tertiary proton and the adjacent ring protons have very nearly the same chemical shift as in the 2,4- and *exo*-olefin, the doublet is poorly resolved and appears to contain some lines between the two major lines.

Acknowledgment.—This work was supported in part by a departmental National Science Foundation undergraduate summer grant, support for which we are grateful. We appreciate help during the early stages from Jeanne Allen and F. Allen Morehead, Jr.

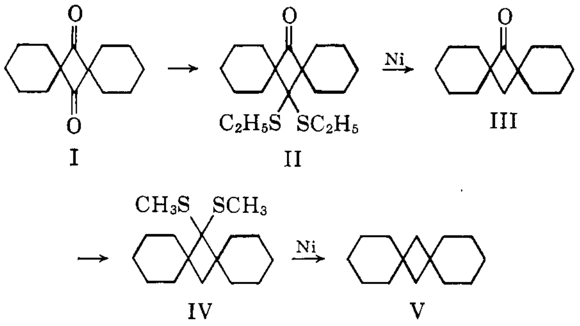
Synthesis and Identification of Dispiro[5.1.5.1]tetradecane[1]

PAUL F. DONOVAN, SHIRLEY A. LIEBMAN, AND STANLEY D. KOCH

Monsanto Research Corporation, Boston, Massachusetts

Received September 5, 1962

Walborsky and Buchman[2] reported the synthesis of dispiro[5.1.5.1]tetradecane from cyclohexyl ketene dimer according to the following reaction sequence.



An attempt to reproduce their work led to the isolation of compounds IV and V in higher yields than they reported and with different physical properties. Chemical and instrumental evidence are presented to show that the hydrocarbon of properties described in this work is dispiro[5.1.5.1]tetradecane.

The attempt to reproduce Walborsky and Buchman's work gave results in reasonable agreement with those reported through compound III, dispiro[5.1.5.1]tetradecan-7-one. However, the dithioketal (IV) was obtained in 76% yield as a solid melting at 117–119°, while Walborsky and Buchman reported a 48% yield of a solid melting at 83.5–84.5°. Dispirotetradecane (V) was obtained in 86% yield as a solid melting at 56.5–58°, rather than the reported 17% yield of a liquid boiling at 131° (10 mm.), m.p. 10°.

Several other approaches to the synthesis were attempted. Buchman and Herzog[3] earlier reported a successful Wolff–Kishner reduction of the disemicar-

---

[6] See ref. 5, p. 95.

[7] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 301.

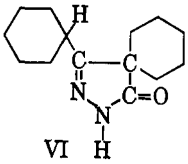
[8] F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

[1] This work was presented before the Division of Organic Chemistry at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

[2] H. M. Walborsky and E. R. Buchman, *J. Am. Chem. Soc.*, **75**, 6339 (1953).

bazone of dimethyl ketene dimer[3] and Walborsky and Buchman had suggested[2] that such an approach might be applicable to cyclohexyl ketene dimer I. Following this suggestion, some work was directed toward the preparation of the disemicarbazone of I, but only the monosemicarbazone was formed, in 94% yield. This appeared to illustrate steric interference by the flanking, nonplanar cyclohexyl rings. Such steric interference has been suggested by Walborsky[4] to explain why the two carbonyl groups of I cannot be converted simultaneously to dithioketal groups.

An alternate Wolff–Kishner approach for the reduction of the diketone I, utilizing a special procedure[5] for sterically hindered carbonyl groups, was investigated. This approach called for intermediate hydrazone formation followed by *in situ* reduction. Despite vigorous reaction conditions, the product was a 5-pyrazolone (VI) (isolated in 77% yield). An analogous pyrazolone was reported from the reaction of hydrazine on 2,2,4,4-tetramethylcyclobutadione-1,3.[6]



VI

Another possible structure for VI, that of a monohydrazone of I, was ruled out since VI had been isolated from a reaction medium conducive to Wolff–Kishner reduction. In addition, the infrared spectrum of VI strongly supports the assigned pyrazolone structure.

An attempt to prepare V *via* the ditosylate of dispiro[5.1.5.1]tetradecane-7,14-diol was abandoned after several attempts at detosylation using lithium aluminum hydride in tetrahydrofuran were unsuccessful.

Instrumental Evidence for the Structure Assignment of V.—The infrared spectrum of dispiro[5.1.5.1]-tetradecane-7,14-dione (I) was determined. Cyclohexyl methylene stretching vibrations were found at 2920 and 2841 cm.$^{-1}$, carbonyl stretching at 1742 cm.$^{-1}$, methylene bending at 1445 cm.$^{-1}$, and additional bands at 984 (m), 915 (w), and 864 (w) cm $^{-1}$ were noted. The methylene stretching and bending vibrations appeared in the regions reported[7] for those in six-membered rings. The bands at 984, 915, and 864 cm.$^{-1}$ resemble the pattern of peaks found in the spectra of some 1,1-disubstituted cyclohexyl compounds[8] and seen in the infrared spectra of the following related compounds: spiro[5.5]undecane 990 (m), 910–890 split (m), 850 (m); spiro[4.5]decane 990 (w), 940 (m), 850 (m)[9]; dispiro[5.1.5.0]tridecane 943 (s), 900, 880 (m), 855, 845 (m)[10,11]; and 7,7-bis(methylmercapto)dispiro[5.1.5.1]-tetradecane (IV) 945 (m), 905 (w), 855 (m) cm.$^{-1}$. This band pattern is variable in 1,1-disubstituted cyclohexyl systems and gives only limited information unless substantiated by other investigations.

The anomalous carbonyl stretching frequency of 1742 cm.$^{-1}$ in the spectrum of the diketone I was studied further. Carbonyl frequencies of the following related compounds were compared to illustrate structural influences which may account for this low absorption frequency: cyclobutanone (VII), 1788 cm.$^{-1}$; III, 1767 cm.$^{-1}$ (with weak shoulder at 1724 cm.$^{-1}$); tetramethyl-1,3-cyclobutadione (VIII), 1761 cm.$^{-1}$ (secondary band at 1727 cm.$^{-1}$); I, 1742 cm.$^{-1}$ (weak shoulder at 1701 cm.$^{-1}$). These frequencies were obtained from spectra run in this laboratory on carbon tetrachloride solutions of the ketones, except for cyclobutanone.[12] The comparison shows that there is an average decrease of 20 cm.$^{-1}$ going from a carbonyl in a simple four-membered ring to one in a four-membered ring perturbed by two spiro linkages (comparing VII to III and VIII to I). There is an average decrease of 26 cm.$^{-1}$ going from a cyclobutanone to a cyclobutadione, with or without the spiro linkage (comparing VII to VIII and III to I). This series illustrates two structural features which may account for the decrease of 46 cm.$^{-1}$ of the carbonyl band in I relative to that in VII: *the presence of the two spiro linkages, and* interaction between the two carbonyl groups. While this manuscript was in preparation, LaLancette and Benson[13] showed ultraviolet spectral data substantiating possible 1,3 π-interaction in tetramethyl-1,3-cyclobutadione (VIII).

Dispiro[5.1.5.1]tetradecane (V) was estimated to be at least 99.5 area % pure by v.p.c.

The infrared spectrum in carbon tetrachloride solution showed strong C—H stretching absorptions at 2920–2850 cm.$^{-1}$, C—H bending at 1447 cm.$^{-1}$, and a well developed side peak at 1430 cm.$^{-1}$. Since this shoulder is absent in the diketone, weak in the monoketone, and of medium intensity in the dispirotetradecane, the cyclobutyl methylene bending absorption is thought to be responsible.

Absorption bands at 948 (m), 939 (m), and 848 (m) cm.$^{-1}$ were of added interest, since these are in the region of reported cyclobutyl ring deformation absorptions.[14,15] Absorptions attributed to five- and six-membered alicyclics have also been shown to appear rather consistently in this region.[16] Monosubstituted cyclohexyl rings exhibited peaks near 850 and 900 cm.$^{-1}$. This absorption varied throughout the 900–1000-cm.$^{-1}$ range for disubstituted cyclohexanes. It is evident that absorptions due to other groups overlap the region assigned for the cyclobutyl group. In the spectrum of V, the 848-cm.$^{-1}$ band probably is due to the six-membered rings and those at 939, 948 cm.$^{-1}$

---

[3] H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

[4] H. M. Walborsky, *ibid.*, **18**, 702 (1953).

[5] D. H. R. Barton, A. A. J. Ives, and B. R. Thomas, *J. Chem. Soc.* 2056 (1955).

[6] R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).

[7] N. Jones and C. Sandorfy in "Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," W. West, Ed., Interscience, New York, N. Y., 1956, pp. 247, 365.

[8] S. A. Liebman, P. F. Donovan, and S. D. Koch, *J. Org. Chem.*, **27**, 4636 (1962).

[9] J. A. Dixon and P. A. Naro, *ibid.*, **25**, 2094 (1960).

[10] S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961).

[11] S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, *J. Org. Chem.*, **26**, 3122 (1961).

[12] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1228 (1961).

[13] E. A. LaLancette and R. E. Benson, *ibid.*, **83**, 4867 (1961).

[14] L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

[15] J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

[16] Cyclopentyl compounds at 890 and 930 cm.$^{-1}$, ref. 17, p. 31; cyclopentyl derivatives at about 977 cm.$^{-1}$, ref. 14; bicyclopentyl, bicyclohexyl, seven dicyclopentyl-, and two dicyclohexylalkanes averaging near 895 and 935 cm.$^{-1}$, ref. 18; tricyclopentyl- and 1,3,5-tricyclopentylcyclohexane at 890 and 930 cm.$^{-1}$, unpublished work from this laboratory.

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958, p. 205.

[18] S. V. Markova, P. A. Bazhulin, A. F. Plate, and V. I. Stanko, *Opt. and Spectry. (USSR)* (Eng. Transl.), **8**, 260 (1960).

may be cyclobutyl ring deformation or additional peaks from the 1,1-disubstituted cyclohexyl rings. The latter do not establish unequivocably the presence of the cyclobutyl ring without further substantiation.

Since Wiberley and co-workers[19] quoted variations in C—H stretching absorptions for three-, four-, five-, and six-membered alicyclics, closer examination of the 3300–2700-cm.$^{-1}$ region was made with lithium fluoride optics. Cyclobutyl C—H stretching bands have been assigned[20] near 2985 and 2907 cm.$^{-1}$ for the asymmetric and symmetric vibrations, respectively. In the spectrum of V, peaks were found at 2923 (s), 2855 (m), and 2842 (m) cm.$^{-1}$. The 2923- and 2855-cm.$^{-1}$ bands correspond to the respective asymmetric and symmetric C—H stretching vibrations of the cyclohexyl methylene groups, but the 2842-cm.$^{-1}$ peak is well below the frequency expected for cyclobutyl methylene groups. In the lithium fluoride infrared spectrum of a homologous compound, dispiro[5.1.5.0]tridecane, the cyclopropyl methylene C—H asymmetric and symmetric stretching vibrations appeared 30 to 40 cm.$^{-1}$ lower in frequency than those assigned in the literature.[10] A similar shift may take place with the cyclobutyl C—H frequencies in dispiro[5.1.5.1]tetradecane, resulting in revised expected frequencies near 2950 and 2870 cm.$^{-1}$. However, heavy cyclohexyl bands partially overlap these frequency ranges. Thus the 2842-cm.$^{-1}$ band required further investigation and lithium fluoride infrared spectra were obtained for compounds I and III. The dione exhibited cyclohexyl C—H bands at 2923 and 2848 cm.$^{-1}$ and the monoketone at 2928 and 2855 cm.$^{-1}$ with no noticeable shouldering seen near 2840 cm.$^{-1}$. The 2848-cm.$^{-1}$ peak in the dione spectrum was intermediate between the 2855-, 2842-cm.$^{-1}$ doublet seen in V. The appearance of roughly equal intensity peaks on either side of the unperturbed vibration indicates that a common Fermi resonance effect may be present.

It is concluded from the evidence in the 3300–2700-cm.$^{-1}$ region that the cyclobutyl C—H stretching bands in V are obscured by the strong cyclohexyl absorptions and that the cyclohexyl symmetric stretching absorption is complicated by Fermi resonance.

A Raman spectrum of V was obtained for comparison with the infrared spectrum and for evidence of cyclobutyl ring-breathing absorptions. No genuine coincidences in the Raman and infrared spectra were observed below 1700 cm.$^{-1}$. This suggests, by the rule of mutual exclusion, that the molecule possesses a center of symmetry. The over-all simplicity of the infrared spectrum also indicates a highly symmetrical form, considering that there are 108 vibrational degrees of freedom for the $C_{14}H_{24}$ hydrocarbon. Any projected rearranged products arising from this synthesis route would be expected to have less symmetry and to show a richer spectrum throughout the 1500–650-cm.$^{-1}$ region.

If Batuev's[21] ring-coupling treatment were followed for the cyclobutyl ring-breathing vibration, the observed peaks in the Raman spectrum of V near 990 and 945 cm.$^{-1}$ would give a mean frequency of 968 cm.$^{-1}$. The unperturbed cyclobutane vibration is assigned at 970 cm.$^{-1}$.[7] However, additional comparison spectra with model dispiranes are needed before such a treatment could be used for structural evidence.

The nuclear magnetic resonance spectrum of V provided final conclusive evidence of the proposed dispirotetradecane structure. It has only two peaks: one at τ 8.62 corresponding to cyclohexyl protons, and one at τ 8.52 showing a shift from the literature value of τ 8.04 for cyclobutyl protons.[12] However, increased shielding of the latter protons by the cyclohexyl rings in this structure could reasonably cause a shift of the observed amount and direction. The homolog dispiro[5.1.5.0]tridecane showed[11] a chemical shift of τ 10.01 for the cyclopropyl protons, compared to literature values of τ 9.78.[12,22] The observed signal for these cyclopropyl protons was at higher field than that for previously reported methylene protons in organic compounds, while the cyclohexyl proton signal was at τ 8.58, close to the usual value.

The sharp, symmetrical shape of the ring proton peaks in the n.m.r. of V follows Chamberlain's observation[23] that saturated alicyclics produce sharp bands if unsubstituted or *gem*-disubstituted, while lower degrees of substitution result in unresolved broad bands at 30 or 40 Mc. The observed lack of multiplet structure from spin–spin coupling in the 40- and 60-Mc. spectra would be anticipated since the cyclobutyl protons are adjacent to quaternary carbon atoms. This absence of multiplicity also was noted in the n.m.r. spectra of 1,1′-dimethylbicyclohexyl[8] (60 Mc.) and dispiro[5.1.5.0]tridecane[11] (40 Mc.), both of which have two quaternary carbon atoms adjacent to their respective group protons. In the spectrum of the dispirotetradecane (V), the two observed peaks were in a ratio of approximately 4.5:1 (average of four determinations), compared to the theoretical value of 5:1.

Experimental

Infrared spectra were obtained with a Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride optics. Frequencies were checked with a polystyrene film reference and estimated to be accurate and reproducible to 0.01 μ. Other infrared spectra were obtained for the 2700–3300-cm.$^{-1}$ region with a Cary Model 14 recording spectrophotometer with lithium fluoride optics.

The Raman spectra were determined on a Cary Model 81 Raman spectrophotometer on a concentrated solution of the solid in carbon tetrachloride.

The n.m.r. spectra were determined on a Varian Model V-4300B high resolution spectrometer (40 Mc.) or Model A-60 (60 Mc.) with tetramethylsilane as an internal reference. The solid was dissolved in deuteriochloroform for examination.

Vapor phase chromatograms were determined on a Perkin-Elmer Model 154-C vapor fractometer, equipped with a 6-ft. column of 16% *m*-bis(*m*-phenoxyphenoxy)benzene on 35–80-mesh Chromosorb W, operating at 190°, 15-p.s.i. inlet pressure, 100-cc./min. helium outlet flow.

Dispiro[5.1.5.1]tetradecan-7-one (III).[2]—The preparation was based on the work of Walborsky and Buchman.[2] The intermediates had the following properties: dispiro[5.1.5.1]tetradecan-7,14-dione (I), m.p. 163–164°, lit.[2] m.p. 164–165°, 58% yield; 14,14-bis(ethylmercapto)dispiro[5.1.5.1]tetradecan-7-one (II), m.p. 58–59°, lit.[2] m.p. 57.5–58.3°, 81% yield; dispiro[5.1.5.1]tetradecan-7-one (III),[2] m.p. 85–87°, from acetoni-

---

(19) S. E. Wiberley, S. C. Bunce, and W. H. Bauer, *Anal. Chem.*, **32**, 217 (1960).

(20) R. P. Stein, B. S. thesis, Rensselaer Polytechnic Institute, 1958; *cf.* ref. 19.

(21) M. I. Batuev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 3 (1947).

(22) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 52; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 236; S. Brownstein, *Chem. Rev.*, **59**, 472 (1959).

(23) N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

trile, lit.[2] m.p. 89–90.5°, 2,4-dinitrophenylhydrazone, m.p. 183–184°, lit.[2] m.p. 181–182°.

Infrared absorption bands, in cm.$^{-1}$, for diketone I: 2920 (s), 2841 (m), 1742 (s), 1701 (w), 1445 (m), 1357 (w), 1305 (m), 1176 (s), 1136 (w), 1033 (w), 984 (m), 915 (w), 864 (w); for monoketone III: 2920–2850 (s), 1767 (s), 1724 (w), 1445 (s), 1430 (w), 1346 (w), 1220 (w), 1155 (w), 1124 (m), 1031 (w), 995–980 (m), 926 (m), 860 (w), 840 (w).

The diketone I gave only a monosemicarbazone, isolated in 94% yield as tiny white needles, m.p. 210–212°, from 50% ethanol. Its infrared spectrum was consistent with its assigned structure.

Anal. Calcd. for $C_{15}H_{23}N_3O_2$: C, 64.9; H, 8.3; N, 15.1. Found: C, 65.2; H, 8.6; N, 15.1.

7,7-Bis(methylmercapto)dispiro[5.1.5.1]tetradecane (IV).[2]—A Pyrex bomb containing freshly fused zinc chloride (13.4 g., 0.098 mole), ketone III (24 g., 0.116 mole), anhydrous sodium sulfate (13.4 g., 0.094 mole), and methyl mercaptan (123.2 g., 2.56 moles) was allowed to stand at room temperature for 48 hr. with occasional shaking. The excess mercaptan was allowed to boil off and the residue was extracted with ice–water and ether. The ether extract was washed with cold 5% aqueous sodium hydroxide solution, then with water. After drying over sodium sulfate, the ether was removed under reduced pressure. Crude solid, m.p. 111–114°, was recrystallized from acetonitrile to give 25.1 g. (76%) of IV, m.p. 117–119°.

Walborsky and Buchman[2] reported a 48% yield for this compound and a melting point of 83.5–84.5°. They did not report a sulfur analysis for their product.

Anal. Calcd. for $C_{16}H_{28}S_2$: C, 67.6; H, 9.9; S, 22.5. Found: C, 67.4; H, 9.9; S, 22.4.

Dispiro[5.1.5.1]tetradecane (V).[2]—The following were combined and refluxed for 48 hr.: dithioketal IV (24 g., 0.084 mole), no. 28 Raney nickel repeatedly washed with ethanol prior to use (720 g.), and 95% ethanol (2000 ml.). The Raney nickel was filtered off. The ethanolic filtrate was concentrated to about half its initial volume and diluted with water. The resultant milky solution was extracted thoroughly with petroleum ether (b.p. 60–90°). The extract was dried over sodium sulfate and solvent removed by distillation. A pale yellow liquid residue resulted, which was distilled under reduced pressure. The product began to distil at 154° (51 mm.), but, since it started to solidify in the condenser, the distillation was halted. The pot residue, which solidified on cooling, and the solid from the condenser weighed 14.0 g. (86% yield of V). After recrystallization from acetonitrile the product melted from 56.5–58°.

Walborsky and Buchman[2] reported a 17% yield of their hydrocarbon and different physical properties. It may be significant that their product was isolated by distillation from sodium, while the use of sodium was avoided during the isolation of this product.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.4; H, 12.6; mol. wt., 192; R_M (molar refractivity), 60.76. Found: C, 87.4, 87.6; H, 12.7, 12.6; mol. wt., 190, 191 (Rast method); R_M, 59.50.

Infrared absorption bands, in cm.$^{-1}$: 2920–2850 (s), 1447 (s), 1430 (m), 1340 (w), 1285 (m), 1245 (w), 1145 (w), 1067 (w), 948 (m), 939 (m), 848 (m).

3-Cyclohexylspiro[cyclohexane-1,4-(2′-pyrazolin-5′-one)] (VI).—The procedure of Barton, *et al.*,[5] was followed, using 10 g. of sodium (0.40 g.-atom), 500 ml. of diethylene glycol, 50 g. of anhydrous hydrazine (1.56 moles), and 30.8 g. of diketone I (0.14 mole). A total of 25.2 g. (77%) of VI, glistening white plates having a bluish luster, m.p. 174–175°, was isolated from ethanol.

Anal. Calcd. for $C_{14}H_{22}N_2O$: C, 71.8; H, 9.5; N, 12.0. Found: C, 72.1; H, 9.5; N, 12.0.

The infrared spectrum (KBr pellet) exhibited N—H stretch at 3185 cm.$^{-1}$ (strong intensity) and at 3067 cm.$^{-1}$ (medium intensity), carbonyl stretch at 1695 cm.$^{-1}$, and broad absorption between 741 and 800 cm.$^{-1}$ attributed to secondary amide N—H deformation.[17]

To rule out the possibility that VI contained a primary amide group, it was subjected to N-methylation according to the procedure of Loudon and Ogg[24] applicable to cyclic amides. The crude reaction product, a yellow oil, showed about 15 area % of unchanged VI by v.p.c. A portion of the major reaction product was trapped out from the column and its infrared spectrum obtained. There was no absorption in the N—H stretch region, nor in the amide N—H deformation region, supporting the structure assignment of VI. The carbonyl absorption shifted very slightly toward higher frequency (1698 cm.$^{-1}$).

Dispiro[5.1.5.1]tetradecane-7,14-diol.—The procedure used by Walborsky[4] to prepare dispiro[4.1.4.1]dodecane-6,12-diol was adapted for the preparation, using a solution of lithium aluminum hydride (4.7 g., 0.125 mole) in 700 ml. of anhydrous ether, and 55 g. of diketone I (0.249 mole). After recrystallization from benzene–ligroin, 37 g. (66%) of VII was obtained, m.p. 174–175°.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 74.9; H, 10.8. Found: C, 75.0; H, 10.9.

cis–trans isomers are possible for the diol but no effort was made to determine whether it was the *cis* or *trans* glycol (*cf.* Walborsky[4]). However, after initial acidification of the hydrolysate, the aqueous phase had remained slightly turbid. It was made strongly acid with 6 *N* sulfuric acid, and again extracted with ether. This latter extract was worked up separately and provided 0.2 g. of a solid melting at 198–200°, presumably a higher-melting isomer.

Ditosylate of Dispiro[5.1.5.1]tetradecane-7,14-diol.—The procedure of Marvel and Sekera[25] was modified and adapted for this preparation. From 20.3 g. of diol was obtained 47.7 g. of crude ditosylate (darkens at 135°, m.p. 210–220°). Although this yield was nearly quantitative, attempts to recrystallize led to considerable loss of product. From tetrahydrofuran two crops were obtained: 8.7 g. of small, white, felted needles, m.p. 224–225° (clear brown melt); and a second crop, 6.5 g. of small lustrous plates, m.p. 238–240° (clear melt, not darkening until several degrees above the melting point). The high- and low-melting forms of the ditosylate can be accounted for on the basis of *cis–trans* isomerism. No effort was made to identify the specific stereoisomers. The yield of isolated, purified product was 15.2 g. (31%).

Anal. Calcd. for $C_{28}H_{36}O_6S_2$: C, 63.1; H, 6.8; S, 12.0. Found for low-melting form: C, 63.5; H, 6.8; S, 12.3. Found for high-melting form: C, 63.2; H, 6.8; S, 12.0.

Acknowledgment.—This work was supported by Materials Central, Aeronautical Systems Division, U. S. Air Force, under contract AF 33(600) 38448. We wish to thank Professors Richard C. Lord of the Massachusetts Institute of Technology and Wilbert H. Urry of the University of Chicago for valuable consultation and assistance, and Messrs. J. V. Pustinger and William R. Smith for assistance in determination and interpretation of spectra.

---

(24) J. D. Loudon and J. Ogg, *J. Chem. Soc.*, 739 (1955).

(25) C. S. Marvel and V. C. Sekera, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 366.

Tautomerism of 5a,11a-Dehydro-7-chlorotetracycline. Preparation of 5-Alkoxy-7-chloroanhydrotetracyclines

M. SCHACH VON WITTENAU, F. A. HOCHSTEIN, AND CHARLES R. STEPHENS

Medical Research Laboratories, Chas. Pfizer & Company, Inc., Groton, Connecticut

Received March 4, 1963

In 1958 McCormick and co-workers[1] reported the isolation of a microbial metabolite, which was shown to be a dehydro analog of the antibiotic chlorotetracycline[2,3] (**1a**). This metabolite was produced by a blocked mutant of *Streptomyces aureofaciens.* On

---

(1) J. R. D. McCormick, P. A. Miller, J. A. Growich, N. O. Sjolander, and A. P. Doerschuk, *J. Am. Chem. Soc.*, **80**, 5572 (1958).

(2) B. M. Duggar, U. S. Patent, 2,482,055 (1949).

(3) C. R. Stephens, L. H. Conover, R. Pasternack, F. A. Hochstein, W. T. Moreland, P. P. Regna, F. J. Pilgrim, K. J. Brunings, and R. B. Woodward, *J. Am. Chem. Soc.*, **76**, 3568 (1954).