then treated with 200 ml of saturated NH_4Cl solution. The ether layer was separated, washed six times with 75-ml portions of water and once with 75 ml of saturated NaCl, and dried. Concentration *in vacuo* afforded 13.5 g of oil which was dissolved in 250 ml of anhydrous methanol. To this was added a solution of 30 g of NaOH in 350 ml of water, and the resulting mixture was heated at reflux under nitrogen for 16 hr. After cooling, the mixture was extracted with ether. The ether extract was washed with water, 3 *M* HCl, and saturated NaCl solution, and then dried. Concentration *in vacuo* followed by distillation through a 10-cm Vigreux column afforded 1.985 g (14%) of **6b** as a colorless liquid, bp 97–117° (0.6–0.65 mm). This material was characterized by conversion to the 2,4-dinitrophenylhydrazone derivative, which, after recrystallization from ethanol–ethyl acetate had mp 194.0–195.5°, undepressed on admixture with material prepared *via* the isoxazole route above.

Preparation of Keto Ester 4b.—An ether solution of magnesium enolate **2** was prepared under nitrogen by cuprous chloride catalyzed reaction between 89.9 mmol[8] of methylmagnesium iodide and 8.04 g (83.6 mmol) of 2-cyclohexenone (**1**), as described above in the preparation of **6a**. A solution of 8.37 g (83.6 mmol) of ethyl acrylate in 50 ml of ether was then added in one portion at ice-bath temperature, and the mixture was allowed to stir at room temperature under nitrogen for 30 min. The resulting mixture was next treated with dilute aqueous HCl. The ether layer was separated, washed five times with 100-ml portions of water and once with 100 ml of saturated NaCl solution, and dried. Concentration *in vacuo* afforded 15.19 g of amber oil which was distilled through a 10-cm Vigreux column to give 0.45 g (5%) of 3-methylcyclohexanone, bp 25° (0.25 mm), which was identified by spectroscopic comparison with an authentic sample.

The fractional distillation also afforded 2.94 g (17%) of keto ester **4b** as a pale yellow liquid, bp 88–93° (0.1–0.35 mm). Redistillation afforded the analytical sample as a colorless liquid: bp 100–102° (0.45–0.55 mm); ir (neat) 1711 (ketone C=O) and 1735 cm^{-1} (ester C=O); mass spectrum (70 eV) *m/e* 212 (M^+).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.94; H, 9.41.

Registry No.—**4b**, 36794-99-7; **6a** DNPH, 36795-00-3; **6b**, 32456-17-0; **6b** DNPH, 36795-02-5; **7**, 36795-03-6; **8**, 36795-04-7; 3-methylcyclohexanone, 591-24-2.

Rotational Isomerism in β,β-Dichlorovinyl Carbonyl Compounds

JAMES B. ELLERN[1] AND HARRY B. GRAY*

Contribution No. 4517 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109

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In connection with a synthetic effort, we have prepared several of the title compounds, $Cl_2C{=}CHCOX$, where X = H (**1**), Cl (**2**), CH_3 (**3**), and OCH_3 (**4**).[2] These compounds show two bands in the carbonyl-stretching frequency region of their ir spectra. The studies of Dabrowski and coworkers on the related mono-β-chlorovinyl compounds[3a–c] suggest that this phenomenon is due to s-cis,s-trans[4] isomerism about the olefin–carbonyl bond.

Infrared absorption bands in the 1500–1800-cm^{-1} region and nmr chemical shifts are set out in Table I. Inspection of the ir data suggests that the higher frequency carbonyl band (A) should be assigned to the s-cis forms of the compounds and the lower one (B) to the s-trans form. As one would expect the relative intensity of band A (s-cis) increases with the size of X. Also, the relative strength of band B is usually apparently greater in the more polar solvent.[3b,c] The ketone **3** appears to be a particularly good example. There are four well-resolved double bond stretching bands in CCl_4 and C_2Cl_4; it is tempting to assign the two outer bands to the s-cis form and the two inner ones to the s-trans.[3b] But this simple picture is complicated when one considers all the data, especially for the ketone. In this compound, the relative intensity of band A to band B is in the order $CH_3CN > CH_2Cl_2 > CHCl_3 > CCl_4$, C_2Cl_4. Similarly, a careful inspection of the ester **4** spectra indicates band B is probably actually more intense in CH_3CN. In addition, there are more than two bands in the C=C region for all the compounds.[5] The discussion below considers these facts.

In the aldehyde **1**, band B is much more intense than band A and is relatively stronger in CH_3CN. Since this is the least sterically hindered compound and the s-trans form is electronically favored,[3b] band A is assigned to $\nu_{C=O}$ (s-cis) and band B to $\nu_{C=O}$ (s-trans). The strongest C=C band, 1585 cm^{-1}, is assigned to $\nu_{C=C}$ (s-trans). These s-trans bands are near those found in the s-trans monochlorovinyl aldehyde (1692 and 1588).[3a] The s-cis C=C band is probably overlaid by the s-trans one; both the other bands between 1500 and 1600 cm^{-1} seem too strong to go with the weak s-cis C=O band.

In the acid chloride **2** the two well-resolved C=O bands are of comparable intensity. The relative intensity of band B is markedly greater in CH_3CN. These two bands are therefore assigned as for the aldehyde. Both shoulders on the very strong C=C band increase as band B increases, but, since it is difficult to judge intensities for these closely spaced absorptions, we are reluctant to assign any of them definitely to one conformer or the other.

The ketone **3** departs from the pattern of **1** and **2**. Bands A and B are well separated and of comparable intensity as in **2**, but the relative strength of band B *falls* with increasing solvent polarity. Both the highest and lowest band in the C=C region show the same behavior relative to the strongest C=C band. The Noack criterion, *viz.*, that $\nu_{C=O}$ in s-cis shifts less than that of $\nu_{C=O}$ in s-trans in going from CCl_4 to $CHCl_3$,[6] is no help in this case except that it may suggest that the conformers in this case are not very close to s-cis and s-trans. A quasi-s-trans rotamer must be considerably skewed from planarity in **3** due to interference between the methyl and the nearer β-chlorine.[7]

(1) NSF Predoctoral Fellow, 1966–1970.

(2) Our interest in these compounds stems from our discovery that they react with certain secondary amines to yield directly aminoethynyl carbonyl compounds: ethynylogous amides, "push–pull" acetylenes. *Cf.* H.-J. Gais, K. Hafner, and M. Neuenschwander, *Helv. Chim. Acta*, **52**, 2641 (1969). These results will be communicated shortly.

(3) (a) J. Terpinski and J. Dabrowski, *Bull. Akad. Pol. Sci., Ser. Sci. Chim.*, **17**, 355 (1969); (b) J. Dabrowski and K. Kamienska-Trela, *Bull. Chem. Soc. Jap.*, **39**, 2565 (1966); (c) J. Dabrowski and J. Terpinski, *J. Org. Chem.*, **31**, 2159 (1966).

(4) We recognize that both conformations may deviate from planarity; *cf.* A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. B*, 810 (1969), and D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 365 (1970).

(5) Factors other than rotational isomerism that may cause band splitting (*e.g.*, Fermi resonance) are discussed in ref 3b and c and references cited therein; see also ref 8.

(6) K. Noack, *Spectrochim. Acta*, **18**, 1625 (1962).

(7) (a) A sketch made to scale using reasonable values for bond lengths and contact radii (values from Pauling[7b]) or the use of models shows this; (b) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

TABLE I

SPECTRAL DATA FOR THE COMPOUNDS $Cl_2C{=}CHCOX$

X	Solvent	Ir absorption bands, cm^{-1} C=O[a]	Ir absorption bands, cm^{-1} C=C[a]	Nmr (δ)
H	CCl_4	1733 (w, shp) (A) 1688 (vs) (B)	1591 (s, sh) 1585 (s) 1569 (m)	6.25 (d, 1, J = 6.7 Hz, $Cl_2C{=}CH$) 9.56 (d, 1, J = 6.7 Hz, -CHO) (neat liquid)
	CH_3CN	1727 (w, brd) (A) 1687 (vs) (B)	1595 (s, sh) 1585 (s) 1570 (m, sh)	
Cl	CCl_4	1789 (s) (A) 1766 (s–vs) (B)	1575 (s, sh) 1570 (vs) 1557 (m, sh)	6.72 (s) (neat liquid)
	CH_3CN	1790 (m–s) (A) 1765 (vs) (B)	1576 (vs, sh) 1571 (vs) 1558 (m–s, sh)	
CH_3	CCl_4	1708 (s) (A) 1678 (m–s) (B)	1585 (s) 1577 (s, sh) 1574 (vs) 1557 (m, sh)	2.03 (s, 3, CH_3) 6.42 (s, 1, $Cl_2C{=}CH$) (neat liquid)
	C_2Cl_4	1707 (s) (A) 1676 (m–s) (B)	1583 (s) 1576 (s, sh) 1571 (vs) 1557 (m, sh)	
	$CHCl_3$	1701 (s) (A) 1671 (m–s) (B)	1584 (s) 1576 (s, sh) 1572 (vs) 1560 (m)	
	CH_2Cl_2	1702 (s) (A) 1673 (m–s) (B)	1584 (s, sh) 1576 (vs, sh) 1572 (vs) 1557 (m)	
	CH_3CN	1703 (s) (A) 1673 (m)	1587 (s, sh) 1574 (vs) 1569 (vs, sh) 1557 (m)	
OCH_3	CCl_4	1742 (vs) (A) 1718 (s)[b] (B)	1617 (m, sh) 1608 (vs)	3.59 (s, 3, OCH_3) 6.29 (s, 1, $Cl_2C{=}CH$) (neat liquid)
	CH_3CN	1733 (vs) (A) 1718 (s–vs, sh)[b] (B)	1618 (s, sh) 1609 (vs)	

[a] These designations refer to the generally accepted spectral regions and do not necessarily imply assignment; see discussion below. [b] The integrated intensity is probably actually greater in CCl_4.

Even in *trans*-4-chloro-3-buten-2-one, the s-trans conformer is not quite planar[3c] and the mesityl oxide is all s-cis.[6] It is noteworthy that band A in **3** is at higher, and band B at lower, frequency than in the monochlorovinyl ketone under the same conditions (C_2Cl_4 solution).[3b] It thus appears that at least one of the rotamers of **3** has a different nature from those of the monochloro ketones and possibly different from those of **1** and **2**.[8] Both the slightly smaller size of chlorine compared to methyl[7b] and differences in electronic structure probably account for the spectral differences between **2** and **3**.

Considerations similar for those for **3** may apply to the ester **4**. Changes in intensity are more difficult to gauge in **4** compared to **3**, and there is a lack of data on the related monochlorovinyl compounds.[9]

Overall we conclude that the compounds studied all show rotational isomerism. The exact nature of the conformers is however unclear, especially as X becomes large. A recently described matrix isolation technique might help elucidate this problem.[10]

(8) After the submission of this note, we found that we had overlooked a differing interpretation of the spectrum of the ketone **3** in the literature. Based on a film spectrum and the dipole moment of **3**, Searles, *et al.*, regard **3** as all quasi-s-trans: S. Searles, Jr., R. A. Sanchez, R. L. Soulen, and D. G. Kundiger, *J. Org. Chem.*, **32**, 2655 (1967). They assert band B is an overtone of the strong unsplit (in their spectrum) C–Cl band at 833 cm^{-1}. We re-examined our spectra with the following results and conclusions. In CS_2 and CCl_4 band B is more intense than the C–Cl absorption and the latter is split in CS_2 (832 and 817 cm^{-1}). There is no absorption near 785 cm^{-1}; thus the splitting of the C=C absorption cannot be due to Fermi resonance or an overtone. We believe it unlikely that s-trans **3** would have its C=O absorption ~20 cm^{-1} *higher* than s-trans **1** unless the former is highly skewed (and therefore effectively nonconjugated), a conclusion the above authors reject. The fact that s-cis **3** might well be *more* polar than the s-trans conformer, as stated by these authors, is consistent with out solvent effect data. Thus, we believe **3** to exist as two conformers, at least in solution. None of the compounds **1**, **2**, or **4** has a strong absorption at one-half the frequency of the weaker carbonyl band.

(9) A. N. Kurtz, W. E. Billups, R. B. Greenlee, A. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965), report only one C=O band for *cis*- and *trans*-3-chloropropenoyl chloride and the methyl esters. However, the resolving power of their instruments was probably less than that of ours.

(10) A. Krautz, T. D. Goldfarb, and C. Y. Lin, *J. Amer. Chem. Soc.*, **94**, 4022 (1972).

Experimental Section

Spectral Analysis.—Ir spectra were taken on a Perkin-Elmer 225 grating infrared spectrophotometer in 0.1-mm KBr cells. Solutions were 50 mg/ml. Nmr spectra were taken on a Varian A-60A analytical nmr spectrometer.

Syntheses.—*Caution.* β-Chlorovinyl carbonyl compounds

should be treated as vesicants. Solutions of 3,3-dichloropropenoate anion generate explosive chloroacetylene on warming.[11] The ketone **3** reacts with concentrated aqueous alkali to yield an explosive gas, probably also HC≡CCl.[12]

3,3-Dichloropropenal (1) was obtained by a reported method:[13] bp 38–39° (21 mm); 2,4-dinitrophenylhydrazone mp 164–165° [lit.[13] bp 85° (35 mm);[14] 2,4-DNP mp 164–165°].

4,4-Dichloro-3-buten-2-one (**3**) was prepared by acetylation of 1,1-dichloroethene,[15a,b] bp 59.5–60.0 (18 mm) [lit. bp 153–156° (atm),[15a] 45° (10 mm), 58° (15 mm)[15b]]. This material is stable at least 8 months at −15° if carefully freed from dissolved HCl by refluxing several hours in a 30-cm Vigreux column under vacuum, distilling (90% of once-distilled material boils within a 0.5° range), and purging the main fraction with nitrogen.

3,3-Dichloropropenoic acid was prepared by the haloform reaction (0–5°) on a mixture of 4,4,1-trichloro-3-buten-2-one and 4,4,4,1-tetrachloro-2-butanone, prepared analogously to **3**, using ordinary chlorine bleach (55% overall yield): white needles from CCl_4; mp 76–77° (lit.[16a,b] mp 76–77°); ir (CCl_4) 1742 (w, sh), 1706 (vs, C=O), 1598 cm^{-1} (vs, C=C); nmr (CCl_4) δ 6.38 (s, 1, Cl_2C=CH), 12.21 (s, 1, COOH); satisfactory analyses for C, H, and Cl.

3,3-Dichloropropenoyl chloride (**2**) was prepared in 75–80% yield by refluxing the acid 1.5 hr with a 75% excess of $SOCl_2$ and fractionating, colorless liquid, bp 51.6–52.2 (18 mm) [lit.[16b] bp 145° (atm)], no $SOCl_2$ by ir.

Methyl 3,3-dichloropropenoate (**4**) was prepared by Fischer esterification of the acid (10% H_2SO_4 in ~20-fold excess CH_3OH, 2-day reflux). Fractionation after the usual work-up gave a 75–80% yield of colorless liquid, bp 57.7–58.8° (18 mm). This compound has mp ~15°; the analytical sample, whose ir spectrum was identical with that of the distillate, was obtained by fractional freezing.

Anal. Calcd for $C_4H_4Cl_2O_2$: C, 31.00; H, 2.60. Found: C, 31.09; H, 2.61.

Registry No.—**1**, 2648-51-3; **2**, 20618-08-0; **3**, 5780-61-0; **4**, 2257-46-7.

(11) O. Wallach, *Justus Liebigs Ann. Chem.*, **203**, 83 (1880), and our observations.

(12) We surmise that this occurs by a reaction analogous to the "acid" cleavage of acetoacetic esters.

(13) M. S. Kharasch, O. Reinmuth, and W. A. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).

(14) In view of the boiling points of the compounds **2–4**, this is almost surely a typographic error in ref 13.

(15) (a) O. Wichterle and J. Vogel, *Collect. Czech. Chem. Commun.*, **19**, 1197 (1954); (b) I. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1430 (1949).

(16) (a) F. Strauss, L. Kollek, and W. Heyn, *Ber.*, **63**, 1868 (1930); (b) O. Wallach, *Justus Liebigs Ann. Chem.*, **193**, 1 (1878).

2,3,4,5-Tetrahydro-1*H*-phosphorino[4,3-*b*]indoles and Derivatives[1]

K. C. SRIVASTAVA[2] AND K. D. BERLIN*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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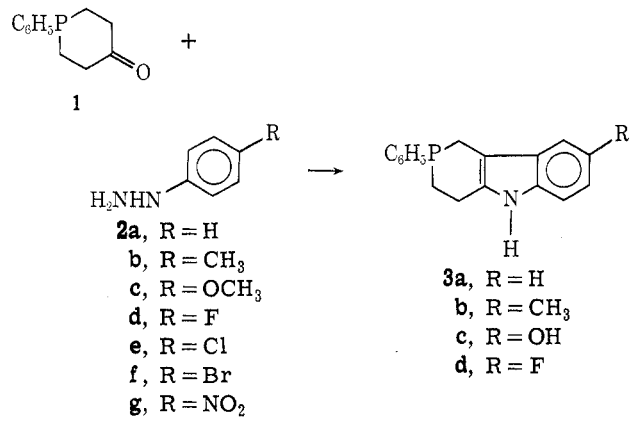
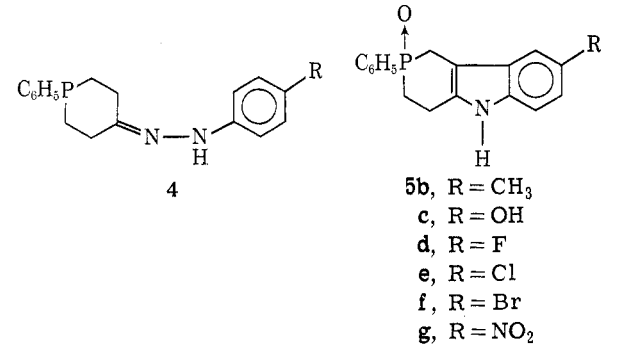
In view of the well-known biological activity of indoles[3,4] and the rarity of 2,3,4,5-tetrahydro-1*H*-phosphorino[4,3-*b*]indoles,[5] and because of our interest in fused C–P ring systems,[6] the need arose for the synthesis of the title class of phosphorus heterocycles. 1-Phenyl-4-phosphorinanone (**1**) was a logical starting material and an improved procedure for its preparation was developed.[7,8]



Condensation of the ketone **1** with various substituted phenylhydrazines **2** or phenylhydrazine hydrochlorides presumably produced phenylhydrazones, which were cyclized *in situ* using glacial acetic acid and concentrated hydrochloric acid[9] to give the corresponding 2,3,4,5-tetrahydro-2-aryl-1*H*-phosphorino-[4,3-*b*]indoles **3a–d**, all high-melting, crystalline solids. It was found that the subsequent indolization occurred readily when the original arylhydrazine had an electron-releasing substituent in the 4 position, as noted in the classic studies with simpler ketones.[10] The presence of a nitro group at the 4 position produces an opposite effect; only the oxide **5g** could be isolated in



low yield. Consequently, the particular hydrazone precursor **4** (R = NO_2) could be isolated and was characterized.

Formation of the corresponding phosphine oxides **5** occurred so rapidly in some condensations (from **2e–g** → **5e–g**) that the phosphines could not be obtained. Their data are reported in Table I along with the other oxides.

Quaternization of 2,3,4,5-tetrahydro-2-aryl-1*H*-phosphorino[4,3-*b*]indole compounds **3** occurs easily to give

(1) We gratefully acknowledge partial support by the National Institute of Health, Cancer Institute, CA 11967-08. We also thank the Research Foundation, Oklahoma State University, for preliminary support. We gratefully acknowledge the National Science Foundation Institution grant to purchase the XL-100 nmr unit, Grant NSF GP-17641.

(2) Research Associate, 1972.

(3) R. V. Heinzelman and J. Szumuszkovicz, "Progress in Drug Research," Vol. 6, E. Jucker, Ed., Birkhauser Verlag, Basel, 1963, p 75.

(4) R. J. Sundberg, "The Chemistry of Indoles," in "Organic Chemistry: A Series of Monographs," Vol. 14, A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1970.

(5) The *P*-phenyl derivative of the parent compound is the only member reported; see M. J. Gallagher and F. G. Mann, *J. Chem. Soc.*, 5110 (1962).

(6) T. E. Snider and K. D. Berlin, *Phosphorus*, **1**, 59 (1971); C. C. Chen and K. D. Berlin, *J. Org. Chem.*, **36**, 2791 (1971).

(7) T. E. Snider, D. E. Morris, K. C. Srivastava, and K. D. Berlin, *Org. Syn.*, submitted.

(8) Pioneering work on the synthesis of this compound was done by R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *J. Amer. Chem. Soc.*, **82**, 4437 (1960).

(9) B. Robinson, *Chem. Rev.*, **69**, 227 (1969).

(10) D. Desaty and D. Keglevic, *Croat. Chem. Acta*, **36**, 103 (1964).