furic acid and silica gel. An orange crystalline solid formed (3.2 g., 76.3%, m.p. 70–75°). Recrystallization from a mixture of 30–60° and 60–90° ligroin (1:1) gave 2.6 g. (62%) of nearly white needles, m.p. 74–76° (lit.[12] m.p. 76°), $\lambda_{C\equiv C}^{Nujol}$ 4.46 μ (2242 cm.$^{-1}$).

AMHERST, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

A New Synthesis of Unsaturated Acids. II. α,β-Olefinic Acids[1,2]

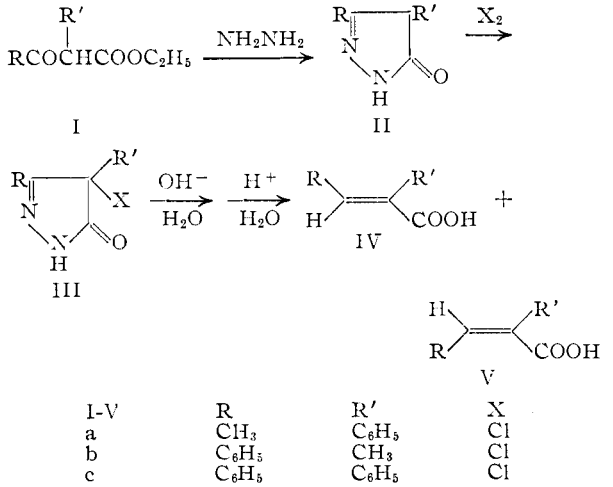
BY LOUIS A. CARPINO

RECEIVED SEPTEMBER 17, 1957

A new synthesis of α,β-olefinic acids is described which involves treatment of a 4-substituted-4-halo-2-pyrazolin-5-one with aqueous sodium hydroxide. While the yield of mixed acids is not exceedingly high (40–65%) the reaction promises to be useful since the labile isomer of the *cis,trans* pair predominates in the mixture. A simple method of separating the isomeric acids, fractional extraction with sodium bicarbonate solution, is described.

In the preceding paper it was shown that the readily available 4,4-dihalo-2-pyrazolin-5-ones were converted by an excess of aqueous alkali at 0–5° to α,β-acetylenic acids in fair to good yields (75–90%). This reaction has now been extended to the corresponding 4-substituted-4-halo compounds since it was expected that the process might lead to a convenient synthesis of α,β-olefinic acids and examination of a pair of isomeric 3,4-disubstituted-4-halo derivatives would yield evidence as to the possibility of cyclopropenone intermediates which was previously considered.

In order to determine whether cyclopropenones intervened in the reaction, 3-methyl-4-phenyl-4-chloro- and 3-phenyl-4-methyl-4-chloro-2-pyrazolin-5-ones (IIIa and IIIb, respectively) were treated with an excess of sodium hydroxide. If cyclopropenones were involved, both IIIa and IIIb should yield the same unsaturated acid. The isolation of IV-Va and IV-Vb, respectively, from these reactions disposes of the possibility of cyclopropenone intermediates.[3] As has been determined by previous workers[4] the acid having the β-substituent and the carboxyl group *trans* to one another is the more stable isomer (IV) of a *cis,trans* pair. Such acids are easily obtainable by the Perkin and Reformatsky reactions. On the other hand, it was found in the present case that a mixture of the *cis,trans* pair was formed in which the labile isomer predominated (see Table I).



I-V	R	R′	X
a	CH_3	C_6H_5	Cl
b	C_6H_5	CH_3	Cl
c	C_6H_5	C_6H_5	Cl

TABLE I

YIELDS OF LABILE AND STABLE ACIDS FROM HALOPYRAZOLONES (%)[a]

Acid	Labile	Stable
α-Phenylcinnamic	35.7 (44.6)	14.7 (17.4)
α-Phenylcrotonic	44.5 (55.5)	8.0 (10.5)
α-Methylcinnamic	21.6 (28)	8.6 (11)

[a] The yield of crude material is given in parentheses.

In view of the ready availability[5] of β-keto esters of all types it would seem that the present reaction represents a useful synthetic route to acids difficult to obtain by other methods.[6] Furthermore by isomerization of the reaction mixture prior to isolation it should be possible to obtain solely the stable isomer although the Perkin and Reformatsky reactions would usually be more suitable providing the requisite aldehydes are available. The 4-halo-2-pyrazolin-5-one precursors are available from the corresponding pyrazolidones[8] as well as from the pyrazolones so that the reaction also can be used as a method of converting the stable isomer IV to

(1) Presented in part at the 132nd National Meeting of the American Chemical Society, September 13, 1957, New York, N. Y.

(2) Supported by the Office of Ordnance Research, U. S. Army.

(3) Several self-evident rationalizations of this reaction are conceivable. Discussion is omitted at the suggestion of the referee since no experimental evidence is available to decide among various possibilities.

(4) See L. Crombie, *Quart. Revs.*, **6**, 101 (1952), for a discussion and review.

(5) Recently several new convenient procedures for the synthesis of β-keto esters have become available: (a) Ester acylations by means of sodium hydride, sodium amide and particularly diisopropylaminomagnesium bromide: E. E. Royals and D. G. Turpin, THIS JOURNAL, **76**, 5452 (1954); F. Y. Swamer and C. R. Hauser, *ibid.*, **72**, 1352 (1950); F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949); J. C. Shivers, M. L. Dillon and C. R. Hauser, *ibid.*, **69**, 119 (1947). (b) Condensation of an α-bromoester with an ordinary ester by means of magnesium: M. Montague, *Bull. soc. chim. France*, 63 (1946) (c) The method of Blaise as modified by Cason, Rinehart and Thornton (ref. 20). (d) Acylation of ketone enamines: G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

(6) Previously two methods have been available for the synthesis of labile acids of type V. Isomerization of the stable acid (IV) by ultraviolet irradiation has been used, although the conversions generally are not high. For example, H. Burton and C. W. Shoppee [*J. Chem. Soc.*, 1156 (1935)] obtained a conversion of 8% by a 70-hour irradiation of *trans*-α-methylcinnamic acid.[7] Recently, a stereospecific method has become available [see *e.g.* (a) A. S. Dreiding and R. J. Pratt, THIS JOURNAL, **76**, 1902 (1954), and (b) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951)].

(7) In this paper *cis* and *trans* refer to the configurations of the parent α,β-unsaturated acids (*e.g.*, V and IV, respectively).

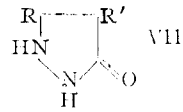
(8) Pyrazolidinone in *Chem. Abstr.* terminology.

the labile form V. For example, the methyl ester of the stable α-phenylcinnamic acid upon treatment with hydrazine hydrate yields the pyrazolidone VI which upon chlorination in nitromethane yields the pyrazolone IIIc.[9]

Initially we experienced considerable difficulty in separating the isomeric *cis,trans*-acids IV and V. Fractional crystallization (ligroin) was without effect. Even the 5:1 mixture IV-Va could not be separated by crystallization since the desired isomer was more soluble in all solvents tested. Previously the benzene-insoluble aniline salt[10] was used to separate the labile α-phenylcinnamic acid from its stable isomer and this method was found to be a useful one for Vc, but IVc could not be obtained quantitatively by working up the filtrates. In the case of the α-phenylcrotonic acids (IV-Va) a modification of Sudborough's[16] partial esterification could be used but again IVa was not quantitatively recoverable as the ester.

TABLE II[a]

CHARACTERISTIC C=O AND C=C[b] INFRARED ABSORPTION BANDS FOR VII AND RELATED COMPOUNDS

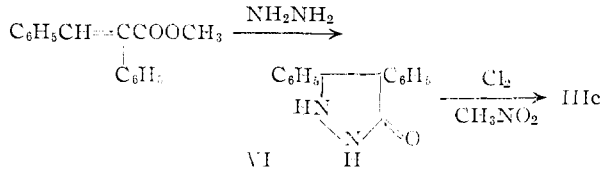


VII

Compound		Position, μ (cm.⁻¹)	
VIIa	(R = C_6H_5, R′ = H)[c]	5.80s	(1724)
		5.97s	(1675)
VIIb	(R = *m*-$O_2NC_6H_4$, R′ = H)[c]	5.80s	(1724)
		5.92m-s	(1689)
VI		5.85m	(1709)
		5.94s	(1684)
VIII	*trans*-$C_6H_5CH{=}CHCOOH$	5.91s	(1692)
		6.11s	(1637)
IX	*trans*-$C_6H_5CH{=}CHCONHN(CH_3)_2$	5.96, 6.01 s	(1678), (1664)
		6.15s	(1626)
X	*trans*-$C_6H_5CH{=}CHCONHN(CH_2C_6H_5)_2$	5.74m	(1742)
		6.00s	(1667)
		6.11s	(1637)
XI	*trans*-*m*-$O_2NC_6H_4CH{=}CHCOOC_2H_5$	5.78s	(1730)
		6.05s	(1653)
		6.16m	(1623)
XII	*trans*-$C_6H_5CH{=}C(CH_3)CONHNH_2$	6.03s	(1658)
		6.17s	(1621)

[a] All spectra are recorded as Nujol mulls. [b] Aromatic C=C absorption (generally weak) is not recorded. [c] See the preceding paper in this series.

Eventually it was found that a simple method is available for the separation of at least the water-insoluble acid pairs which yields both of the acids in the easily recoverable free form. This was achieved by fractional extraction[11,12] by means of sodium bicarbonate solution. In general for a 0.01-mole run we used 10–15 extractions with 10-ml. portions of 0.1 *M* sodium bicarbonate solution.



After acidification, common fractions were combined and worked up in the usual way. On a large scale the method might be tedious although it could be modified by a preliminary small scale run to find the separation point and large scale extracts taken until the separation point is approached. Of the three cases examined the separation procedure worked least well in the case of the α-methylcinnamic acids. This probably was due to the presence of oily by-products.

Experimental[13–15]

4,5-Diphenyl-3-pyrazolidone (VI).—A solution of 23.8 g. of methyl α-phenylcinnamate[16] and 6 g. of hydrazine hydrate in 55 ml. of ethanol was refluxed for 24 hours and cautiously diluted with small amounts of water so as to induce the substance to separate as a solid rather than a heavy oil. In all, about 200 ml. of water was added and the mixture stored in an ice-box 5–6 hours, filtered, washed well with water and air-dried. The yield was 20.9 g., m.p. 116–125°. Recrystallization from about 50 ml. of benzene containing a few drops of nitromethane gave 19.3 g. (81.1%) of small white crystals, m.p. 134–139°. A second recrystallization from the same solvent pair gave 18.8 g. (79%) of the pyrazolidone, m.p. 139–141°.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92. Found: C, 75.90; H, 5.83.

3,4-Diphenyl-4-chloro-2-pyrazolin-5-one (IIIc).—A mixture of 5 g. of VI and 30 ml. of nitromethane was treated with chlorine until an excess was present (15 min.) and the resulting mixture from which the pyrazolone had begun to separate was allowed to evaporate. Recrystallization of the residue from nitromethane gave 3.7 g. (67.4%) of yellow-white crystals, m.p. 163–165° (softening at 150°). Two additional recrystallizations from nitromethane[17] gave 3.2 g. (58.2%) of nearly white crystals, m.p. 170–171° dec. The analytical sample melted at 171.8–173.8° (nitromethane).

(9) This reaction apparently is not completely general, however, since treatment of methyl *trans*-α-methylcinnamate with hydrazine hydrate followed by reaction of the product (see Experimental section) with chlorine did not yield the expected pyrazolone. The ester-hydrazine reaction product is assigned structure XII (Table II) rather than VIIc (R = C_6H_5, R′ = CH_3) on the basis of the reaction with chlorine and the infrared spectral comparisons reproduced in Table II. *trans*-Cinnamic acid shows a strong conjugated C=C absorption at 6.11 μ (1637 cm.⁻¹) and the position and intensity are retained in XII and the trisubstituted hydrazine derivatives IX and X which must have the normal acyclic structure indicated. On the other hand, the 3-pyrazolidones VIIa,b and VI show no strong absorption in this area.

(10) R. S. Stoermer and G. Voht, *Ann.*, **409**, 36 (1915).

(11) Fractional precipitation from carbonate solutions by acetic acid followed by hydrochloric acid has been used to separate IVc and Vc, but in practice we find that this method does not allow a clean separation, at least of the mixture obtained in the present study. See, however, Stoermer and Voht,[10] and L. F. Fieser, *J. Chem. Ed.*, **31**, 291 (1954).

(12) The isomeric α-methylcinnamic acids differ by one power of ten in their ionization constants [R. D. Kleene, F. H. Westheimer and G. Wheland, THIS JOURNAL, **63**, 791 (1941)].

(13) Melting and boiling points are uncorrected.

(14) Analyses are by Drs. Weiler and Strauss, Oxford, England.

(15) Infrared spectra were taken as Nujol mulls and recorded linearly in wave length on a Perkin-Elmer model 21 spectrophotometer, sodium chloride optics. We are indebted to the National Science Foundation and the Research Corporation for funds with which to purchase the spectrophotometer (NSF G-2368).

(16) Prepared by essentially the method of J. J. Sudborough and L. L. Lloyd [*J. Chem. Soc.*, **73**, 81 (1898)] in 86% yield, m.p. 76.5–77.5° (reported m.p. 77°, yield 75%).

(17) In later runs a more efficient method of purifying the crude nitromethane-recrystallized product was developed: 15 g. of the crude material was dissolved in 110 ml. of hot benzene and the solution diluted with 300 ml. of 60-90° ligroin. Filtration after five hours gave 13 g. of the pure, almost white, pyrazolone, m.p. 172–174° dec.

Anal. Calcd. for $C_{15}H_{11}N_2OCl$: C, 66.54; H, 4.09. Found: C, 66.22; H, 3.85.

α-Methylcinnamic Acid Hydrazide.—Methyl α-methylcinnamate was prepared by the method of Edeleano[18] in a yield of 89.5%, m.p. 39–41° (lit.[18] m.p. 39°, yield 83%). A solution of 5 g. of the methyl ester, 1.42 g. of 64% hydrazine and 15 ml. of ethanol was refluxed for 48 hours, diluted to 125 ml. with water, cooled in an ice-box for 5 hours and filtered to yield 2.5 g. (50%) of shiny white crystals, m.p. 60–80°. Recrystallization from ligroin (60–90°)–benzene (1:2) gave 2.0 g. (40%) of soft white flakes, m.p. 105.5–106.5°. The analytical sample from the same solvent mixture melted at 106.5–107.5°.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.15; H, 6.87. Found: C, 68.01; H, 6.94.

This substance was judged not to be 3-pyrazolidone by the fact that treatment with chlorine in methylene dichloride solution did not yield the expected 3-phenyl-4-methyl-4-chloro-2-pyrazolin-5-one (*cf.* the corresponding diphenyl derivative above). Instead an oily substance was obtained which was not examined further except to note that on mixing with dilute aqueous sodium hydroxide no gas evolution was observed.

1,1-Dimethyl-2-*trans*-cinnamoylhydrazine.—A mixture of 12 g. of 1,1-dimethylhydrazine (Metalectro Corp., as received), 27.8 g. of triethylamine and 50 ml. of methylene dichloride was cooled in an ice-bath and 33.4 g. of *trans*-cinnamoyl chloride (Eastman Kodak Co., white label) dissolved in 50 ml. of methylene dichloride was added with efficient mechanical stirring over a period of 1.5 hours. The mixture was stirred for an additional two hours in the ice-bath, washed three times with 50-ml. portions of water and the solvent removed from a water-bath *in vacuo*. The thick oil solidified on trituration with ligroin (60–90°) and the solid was then recrystallized from nitromethane which gave 21 g. (55.2%) of thick white needles, m.p. 105–112°. A second recrystallization from nitromethane gave 18 g. (47.4%) of the pure hydrazide, m.p. 112.5–113.5°.

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42. Found: C, 69.35; H, 7.05.

1,1-Dibenzyl-2-*trans*-cinnamoylhydrazine.—The preparation was carried out in a manner similar to that given above for the 1,1-dimethyl compound except that about 100 ml. of dimethylformamide per 8.33 g. of the acid chloride was used as the solvent. The 1,1-dibenzylhydrazine was prepared by the method of Busch and Weiss.[19] The hydrazide was isolated by precipitation with water. The crude product (82%, m.p. 120–132°) was recrystallized from ethanol (*ca.* 3 ml./g.) which gave lightly cream colored crystals, m.p. 138.5–142°, yield 59%. The analytical sample had m.p. 140.5–142° (ethanol).

Anal. Calcd. for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48. Found: C, 80.38; H, 6.71.

Ethyl α-Methylbenzoylacetate (Ib).—The method of Cason, Rinehart and Thornton[20] was modified by the use of considerably less solvent. Benzonitrile (27.8 g.), 73 g. of ethyl α-bromopropionate (Eastman Kodak Co.), 17.6 g. of 20-mesh zinc, 0.1 g. of cupric bromide and 250 ml. of benzene were employed. The only difference was that the source of heat had to be removed for 10–15 minutes until the initial vigorous reaction subsided. The yield was 24 g. (43%), b.p. 113–116° (0.5 mm.).

3-Phenyl-4-methyl-4-chloro-2-pyrazolin-5-one (IIIb).—The ester Ib was converted to the pyrazolone IIb by the method of v. Auwers and Mauss[21] which gave a 75% yield of crude product, m.p. 212–217°. After recrystallization from water–dimethylformamide (1:1) the yield of long white needles, m.p. 217.5–219.5°, was 65% (lit.[21] m.p. 213–214.5°). A suspension of 17 g. of the recrystallized pyrazolone IIb in 50–60 ml. of nitromethane was heated to boiling and chlorine was passed into the hot mixture until the solid dissolved and a definite excess of chlorine was present (15–20 min.). The mixture was heated occasionally on a hot-plate to keep the halopyrazolone from separating. After standing overnight in an ice-box the solution deposited 14.5 g. of green-yellow needles, m.p. 143–146°. A second recrystallization from nitromethane gave 13 g. of the pure substance, m.p. 144–146°. The filtrates gave an additional 2 g. of pure pyrazolone so that the total yield was 15 g. (70%). Methylene chloride (5 ml./g. of IIb) was also used as solvent for the chlorination. The analytical sample melted at 145.5–146.5° (nitromethane).

Anal. Calcd. for $C_{10}H_9N_2OCl$: C, 57.56; H, 4.35. Found: C, 57.20; H, 4.22.

3-Methyl-4-phenyl-4-chloro-2-pyrazolin-5-one (IIIa).—A suspension of 18 g. of IIa[22] in 100 ml. of methylene chloride was treated with an excess of chlorine and the resulting solution evaporated either spontaneously or from a water-bath with the aid of a water aspirator. The residue was triturated with water, filtered and air-dried. The halopyrazolone (19 g., 88%), m.p. 68–74°, was recrystallized from benzene–60–90° ligroin (1:1) giving 15.5 g. (71.7%) of small white crystals; a second recrystallization gave 14.5 g. (67.1%), m.p. 81–82°.

Anal. Calcd. for $C_{10}H_9N_2OCl$: C, 57.56; H, 4.35; Cl, 16.99. Found: C, 57.40; H, 4.43; Cl, 16.80.

Conversion of 3-Methyl-4-phenyl-4-chloro-2-pyrazolin-5-one (IIIa) to *cis*- and *trans*-α-Phenylcrotonic Acids. Separation of the Isomeric Acids.—A solution of 2.0 g. (0.05 mole) of sodium hydroxide in 50 ml. of water was cooled in an ice-bath and stirred mechanically. There was then added during 1–2 min. 2.0 g. (0.01 mole) of finely powdered IIIa. The clear yellow solution soon became frothy due to gas evolution. Stirring was continued for two hours in the ice-bath and an additional hour at room temperature. The resulting slightly cloudy solution was decolorized with charcoal (J. T. Baker), cooled in an ice-bath and acidified with concentrated hydrochloric acid to congo red. The cream-orange solid which precipitated was extracted with four 25-ml. portions of ether. The combined ether extracts were washed three times with 5-ml. portions of water and fractional extraction with dilute sodium bicarbonate solution was begun. The first extraction was made with 10 ml. of 0.05 *M*. sodium bicarbonate solution in order to remove traces of mineral acid and strongly acidic oily materials occasionally formed as by-products in the reaction. Fourteen additional extractions were then made with 10-ml. portions of 0.1 *M* bicarbonate.[23] Each fraction was then acidified with 0.5 ml. of concentrated hydrochloric acid.

Fraction	Result on acidification
1	No ppt.
2–7	Almost immediate cream-white ppt.
8	Oil ppts. which solidifies in 3–4 minutes
9	Same as no. 8
10–13	Almost immediate cream-white ppt.
14	No ppt.
15	No ppt.

Based on the behavior on acidification, separation was judged to be at fractions 8 and 9 and these were therefore filtered and dried on a clay plate: 8, amt. 0.05 g., m.p. 79–81°; 9, amt. 0.01 g., m.p. 85–110°. Having established the separation point, fractions 2–7 were combined and the acid extracted with four 15-ml. portions of ether, the ether extracts washed once with 5 ml. of water, filtered by gravity to remove any trace of suspended inorganic material and allowed to evaporate. The residue of white-cream crystals amounted to 0.9 g. (55.5%), m.p. 85–90°. Recrystallization from 90–120° ligroin gave 0.72 g. (44.5%) of large creamy flakes, m.p. 94–96.5° (softening at 93°).[24]

(18) L. Edeleano, *Ber.*, **20**, 616 (1887).

(19) M. Busch and B. Weiss, *ibid.*, **33**, 2701 (1900).

(20) J. Cason, K. L. Rinehart and S. D. Thornton, *J. Org. Chem.*, **18**, 1594 (1953); *Org. Syntheses*, **35**, 15 (1955).

(21) K. v. Auwers and H. Mauss, *J. prakt. Chem.*, [2] **110**, 221 (1925). No yield was reported.

(22) S. Veibel, K. Eggersen and S. C. Linholt, *Acta Chem. Scand.*, **8**, 768 (1954). We obtained a yield of 81%; these authors report 30%.

(23) The bicarbonate solutions were prepared by delivering 0.50 and 1.00 ml. of a stock 1 *M* solution from a buret to a graduated cylinder in which the volume was made up to 10 ml. After the separation of each bicarbonate extract 1–2 ml. of water was added as a "chaser" to remove the last portions of each extract and to avoid draining ether into the stopcock bore. Care was taken to equilibrate the layers by shaking for about two minutes after gas evolution stopped. Fifteen extractions required about 1–1.5 hours for completion.

(24) Comparison of this material by its infrared spectrum with the analytical sample showed no difference. A strong band at 14.83 μ (674.3 cm.$^{-1}$), characteristic of the high melting isomer, was absent.

Three additional recrystallizations from 60–90° ligroin gave an analytical sample of pure *cis*-α-phenylcrotonic acid, m.p. 98.5–100°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.25; H, 6.55.

Fractions 10–13 were treated as indicated above for fractions 2–7. Evaporation of the ether gave 0.17 g. (10.5%) of cream colored solid, m.p. 120–131°. Recrystallization from 60–90° ligroin gave 0.13 g. (8.03%) of tiny cream-white crystals, m.p. 134–136.5° (lit.[25] m.p. 135°). The infrared spectrum was identical with that of an authentic sample of *trans*-α-phenylcrotonic acid and showed no significant contamination by the *cis* isomer by the absence of strong bands at 12.80 μ (781.3 cm.$^{-1}$) and 11.70 μ (854.7 cm.$^{-1}$). Fractions 8 and 9 were mixtures containing mainly the *cis*- and *trans*- acids, respectively.

In the present work we tentatively assign structure Va to the compound m.p. 98.5–100° on the basis of method of synthesis (*cf.* the other cases examined here wherein both labile and stable acids have long been known), greater acidity and lesser rate of esterification (see below) compared with its isomer, m.p. 134–136.5°.

Separation of the *cis*-acid was also possible by a modification of the method of Sudborough and Lloyd.[16] A solution of 0.58 g. (78%) of a crude mixture of the *cis* and *trans* isomers obtained from 0.96 g. of IIIa in 5 ml. of a 3% solution of hydrogen chloride gas in commercial absolute methanol was allowed to stand at room temperature for 1.75 hours and then poured into water. Extraction of the precipitated material into ether followed by extraction of the ether solution with several portions of 1 *M* sodium bicarbonate solution served to remove the *cis*- acid from the majority of the *trans*-methyl ester. After acidification and isolation of the crude *cis*-acid (0.45 g., m.p. 88–92°) by means of ether the crude solid was again added to 5 ml. of 3% hydrogen chloride in methanol and allowed to stand for one hour at room temperature. Working up as before gave 0.4 g. (53.9%) of the *cis*-acid, m.p. 92–96° (softening at 88°). Recrystallization from 90–120° ligroin gave 0.26 g. (35%) of snow-white flakes, m.p. 94–98°.

Conversion of 3,4-Diphenyl-4-chloro-2-pyrazolin-5-one (IIIc) to *cis*- and *trans*-α-Phenylcinnamic Acids.—The initial reaction was carried out essentially as indicated above for the corresponding 3-methyl-4-phenyl derivative using 0.01 mole of the pyrazolone. However when fractions 12–14 were reached it appeared that the calculated amount of acid was no longer being extracted. Since the separation point had been passed, the extraction was completed with three 10-ml. portions of 1 *M* bicarbonate. Evaporation of the ether extracts of fractions 2–8 gave 1.0 g. (44.6%) of cream-white crystals, m.p. 123–131° (softening at 100°). Recrystallization from nitromethane gave 0.8 g. (35.7%) of yellow-cream crystals, m.p. 137–139° (lit.[26] m.p. 136–137°).

Fraction 10 and the following were combined and worked up as usual giving 0.39 g. (17.4%) of cream-white crystals, m.p. 160–167° (softening at 155°). Recrystallization from nitromethane gave 0.33 g. (14.7%) of cream colored needles, m.p. 173.5–175° (lit.[26] m.p. 170–172°).

Conversion of 3-Phenyl-4-methyl-4-chloro-2-pyrazolin-5-one to *cis*- and *trans*-α-Methylcinnamic Acids.—The initial reaction of 0.01 mole of the halopyrazolone with alkali was carried out essentially as indicated for the 3-methyl-4-phenyl derivative except that after acidification of the reaction mixture and extraction into ether the mixed acids were then extracted together from the ether solution into about six 20-ml. portions of 1 *M* sodium bicarbonate solution. The bicarbonate extracts were then acidified and the mixed acids again taken into ether and the ether solution then fractionally extracted as: 1–5, 0.05 *M* sodium bicarbonate; 6–10, 0.10 *M* sodium bicarbonate; 11–15, 0.05 *M* sodium bicarbonate; 16–19, 0.10 *M* sodium bicarbonate.

Finally the extraction was completed with four 10-ml. portions of 1 *M* sodium bicarbonate solution. Evaporation of the ether extracts of fractions 5–10 left a slightly oily solid which was dried on a clay plate; 0.45 g. (27.8%) of m.p. 60–85°. Recrystallization from ligroin (60–90°) gave 0.35 g. (21.6%) of well-formed cream-colored crystals, m.p. 86–91°. A second recrystallization gave 0.3 g., m.p. 90–92° (lit.[10] m.p. 91–92°). Evaporation of the ether extracts of fractions 12–20 gave a cream-colored solid which was dried on a clay plate; amount 0.18 g. (11.1%), m.p. 76–79.5° (softening at 74°). Recrystallization from ligroin (60–90°) gave 0.14 g. (8.6%) of tiny cream-colored crystals, m.p. 79–80.5° (lit.[10] m.p. 81–82°).

(25) H. Gilman and S. A. Harris, THIS JOURNAL, **53**, 3541 (1931).

(26) M. Bakunin, *Gazz. chim. ital.*, **27**, II, 48 (1897).

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A Novel Elimination of Acetyl Chloride

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RECEIVED AUGUST 29, 1957

At temperatures below 200°, 2-chloro-3-acyl-*p*-dioxanes (I) decompose to form acid chlorides and *p*-dioxanone. A mechanism is proposed for this reaction. The reaction of 2,3-dichloro-*p*-dioxane with anhydrous formic acid at 170° serves as a convenient laboratory synthesis for *p*-dioxanone. 2-Acetoxy-3-chlorotetrahydropyran does not pyrolyze in a manner similar to the 2-chloro-3-acyl-*p*-dioxanes, but eliminates acetic acid at about 200°.

Discussion

In the course of an investigation concerned with the stereochemistry of 2,3-disubstituted *p*-dioxanes, we were interested in obtaining examples of isomeric pairs of esters of *p*-dioxane-2,3-diol. Several methods of preparation of individual isomers of these compounds are described in the literature. Boeseken and co-workers[1] treated *trans*-2,3-dichloro-*p*-dioxane[2] with potassium acetate or lead acetate in acetic acid and obtained a 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°, of unknown configuration. Another method of preparation is described by Slagh,[3] who treated various acids with *trans*-2,3-dichloro-*p*-dioxane in inert solvents such as toluene and xylene at reflux temperature to prepare the corresponding esters, and claims to have obtained a diacetate having a m.p. of 79°. Hoping that this compound would prove to be the second isomer of 2,3-diacetoxy-*p*-dioxane, we have repeated the work. However, the only compound obtained in several runs was the 2,3-diacetoxy-*p*-dioxane, m.p. 104–105°, identical with that obtained by the method of Boeseken.[1] The treatment of *p*-dioxene with hydrogen peroxide in *t*-butyl alcohol, followed by acetylation of the dihydroxy compound with acetic anhydride and pyridine, resulted likewise in

(1) J. Boeseken, F. Tellegen and P. Cohen Henriquez, THIS JOURNAL, **55**, 1284 (1933).

(2) R. K. Summerbell and Hans E. Lunk, *ibid.*, **79**, 4802 (1957).

(3) Harold R. Slagh, U. S. Patent 2,164,355.