barbituric acid, m. p. and mixed m. p. with the acid obtained from the reduction product of XX 176.5–177°.

Anal. Calcd. for $C_{11}H_{18}O_3N_2$: N, 12.38. Found: N, 12.43.

Ethyl Isopentenyl Allylmalonate (XXI).—Ethyl isopentylidene malonate (57 g.) on alkylation with allyl bromide yielded 61.9 g. (92%) of XXI, b. p. 111–112° (2 mm.); n^{25}_D 1.4437; d^{25}_{25} 0.9615; *M*D calcd. 73.86; found 74.31.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.16; H, 9.15.

When XXI was heated for five hours and then two hours more at 200°, the refractive index increased by only 0.0005 unit during the latter period. Fractionation gave four fractions varying in b. p. from 146 to 151° (15 mm.), and in n^{25}_D from 1.4508 to 1.4581. Further heating of the combined fractions gave similar mixtures, from which a pure rearrangement product could not be isolated. Mixtures were also obtained when XXI was heated at 175°, while at 145° no rearrangement occurred.

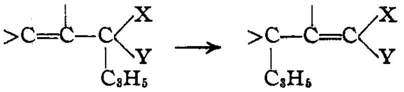
Ethyl 1-Cyclohexenyl Allylmalonate (XXII).—Ethyl 1-cyclohexenylmalonate[23] (80.7 g.) was converted into its sodium enolate with alcoholic sodium ethoxide and alkylated with allyl bromide in the usual manner. The crude product contained an impurity which was removed by shaking with concd. aqueous ammonia, fractionating, again shaking with ammonia and refractionating. The yield of XXII was 39.1 g. (46%), b. p. 109° (0.5 mm.); n^{25}_D 1.4742; d^{25}_{25} 1.0369; *M*D calcd. 76.28, found 76.23.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.72; H, 8.75.

When XXII was heated at 200° for six to twelve hours, a mixture of substances was formed from which the pure rearrangement product could not be separated by fractionation. When the crude isomerization product was shaken with concd. ammonia for a week, a very small amount of 2-allylcyclohexanone was formed. The ketone was isolated by extraction and distillation, and identified by conversion into the oxime, m. p. and mixed m. p. with a known sample 70–70.5°.

Summary

Ten compounds containing structural elements which are represented in the following partial formulas have been shown to isomerize smoothly in the manner indicated on heating to temperatures between 135 and 200°.



$$>C{=}\overset{|}{C}{-}\underset{C_3H_5}{\underset{|}{C}}{<}^{X}_{Y} \longrightarrow >\underset{C_3H_5}{\underset{|}{C}}{-}\overset{|}{C}{=}C{<}^{X}_{Y}$$

(X and Y = CN or COOEt). The double bond may be either acyclic or alicyclic. Kinetic studies have shown that the order of decreasing ease of rearrangement is: malononitriles > cyanoacetic esters > malonic esters. Nine of the ten isomerizations follow the first order kinetic equation, suggesting an intra- rather than an intermolecular mechanism of rearrangement.

BRYN MAWR, PENNSYLVANIA RECEIVED MARCH 27, 1941

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[23] Kon and Speight, *J. Chem. Soc.*, 2731 (1926); Hugh and Kon, *ibid.*, 778 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Rearrangement of Allyl Groups in Three-Carbon Systems. II[1]

BY ARTHUR C. COPE,[2] CORRIS M. HOFMANN AND ELIZABETH M. HARDY

The first report of the rearrangement (α,γ-shift) of an allyl group in a three-carbon system[3] pointed out the structural analogy of this reaction to the Claisen rearrangement. The results described in the preceding paper[4] indicate that the rearrangement is quite general for suitably activated three-carbon systems, just as the Claisen rearrangement is general for the $>C{=}\underset{|}{C}{-}O{-}C_3H_5$ system. This communication describes work undertaken to determine whether substituted allyl groups undergo inversion[5] in the isomerization.

A test of the intra- or intermolecular nature of the reaction was also made, by determining whether an interchange of groups takes place during the simultaneous rearrangement of mixtures.

The occurrence of inversion during the rearrangement was established by preparing ethyl isopropenyl crotylmalonate (I) and ethyl (1-methyl propenyl)-crotylcyanoacetate (II), rearranging these two esters, and determining the structures of the rearrangement products. Preliminary efforts to employ the corresponding esters substituted by cinnamyl rather than crotyl groups failed, for the cinnamyl compounds decomposed during distillation and could not be purified.

The esters I and II were prepared by alkylating ethyl isopropylidenemalonate[6] and ethyl (1-

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[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

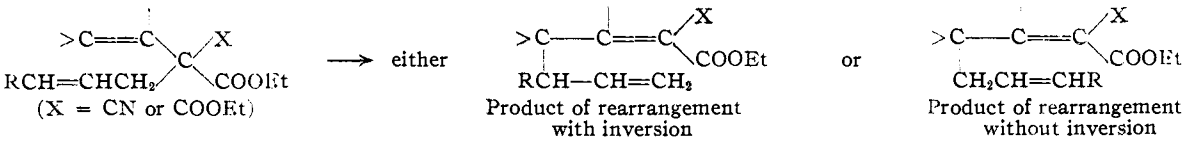
[2] A. C. C. is indebted to the John Simon Guggenheim Memorial Foundation for the award of a fellowship in the general field of this investigation.

[3] Cope and Hardy, THIS JOURNAL, **62**, 441 (1940).

[4] Cope, Hoyle and Heyl, *ibid.*, **63**, 1843 (1941).

[5] *Cf.* Tarbell, *Chem. Rev.*, **27**, 500, 516 (1940), for a discussion of inversion in the Claisen rearrangement.

[6] Cope and Hancock, THIS JOURNAL, **60**, 2644 (1938).



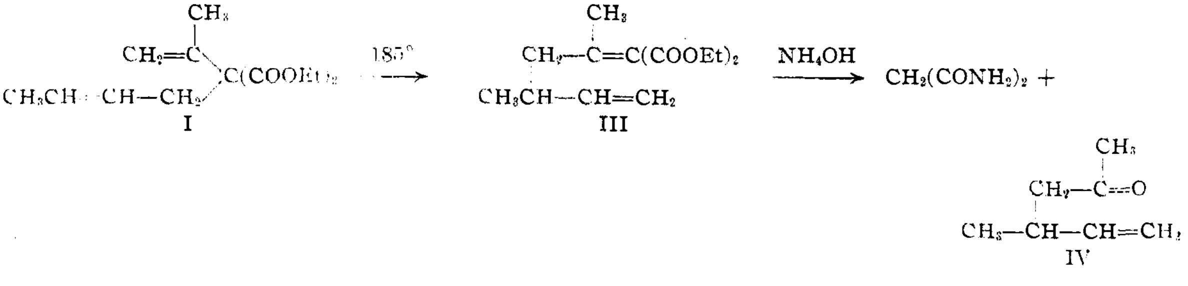
(X = CN or COOEt)

Product of rearrangement with inversion

Product of rearrangement without inversion

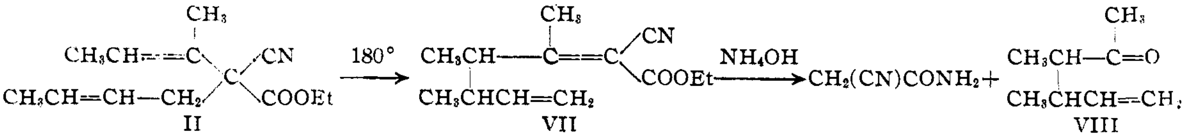
methyl-propylidene)-cyanoacetate[7] with crotyl bromide. It was necessary to prove the structure of each of the alkylation products, for crotyl bromide is in allylic equilibrium with methylvinylcarbinyl bromide,[8] and the synthesis might conceivably proceed with the introduction of methylvinylcarbinyl rather than crotyl groups. The structures of I and II were established by hydrogenation. I on reduction gave ethyl isopropyl butylmalonate, identified by condensation with urea, which produced 5-*n*-butyl 5-isopropylbarbituric acid. II was hydrogenated slowly and incompletely under the conditions employed, and the product isolated on condensing the reduction product with urea was 5-*n*-butyl 5-(1-methylpropenyl)-barbituric acid. The formation of this derivative, whose structure was verified by further reduction to 5-*n*-butyl 5-*s*-butylbarbituric acid, serves to establish the structure of II.

Compound I rearranged smoothly at 185° to give ethyl (1,3-dimethyl-4-pentenylidene)-malonate, III. The structure of III was established by cleavage with concd. aqueous ammonia to the unsaturated ketone IV, which was identified by reduction to 4-methylhexan-2-one (*s*-butylacetone).



I III IV

The ester II rearranged in a similar manner at 180° with inversion of the crotyl group to give ethyl (1,2,3-trimethyl-4-pentenylidene)-cyanoacetate, VII. The structure of VII was established by cleavage with concd. ammonium hydroxide to an unsaturated ketone, VIII, which was identified by reduction to 3,4-dimethylhexan-2-one (*unsym*-*s*-butylmethylacetone).



II VII VIII

In order to test the intra- or intermolecular nature of a rearrangement by the method of rearranging mixtures, two conditions (other than the obvious one that the migrating groups must be different) are necessary. First, the two compounds which are to be rearranged in admixture must isomerize at similar rates, so that there will be opportunity for an interchange of groups; second, the properties of the products of the simultaneous rearrangements should be such as to permit their complete separation, and analysis for homogeneity.

We first sought to find pairs of esters whose isomerization products could be separated by chemical means. Such a separation would appear to be possible if one of the rearrangement products were an alkylidene cyanoacetic ester and the other an alkylidene malonic ester. The former class forms soluble sodium bisulfite addition compounds,[7,9] while the latter does not. This method of separation failed, for the alkylidene cyanoacetic esters produced by rearrangement proved to be insoluble in sodium bisulfite. The rearrangement products are branched and have rather high molecular weights; evidently the reaction of alkylidenecyanoacetic esters with sodium bisulfite is influenced by steric hindrance in a manner similar to the corresponding reaction of ketones.

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[7] Cope and Hancock, THIS JOURNAL, **60**, 2903 (1938).

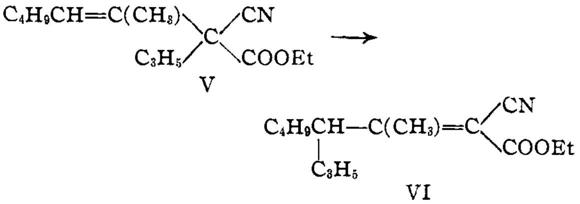
[8] Young and Winstein, *ibid.*, **57**, 2013 (1935), and later papers by Young, *et al.*

[9] Lapworth and McRae, *J. Chem. Soc.*, **121**, 2745 (1922).

Efforts to prepare an ester substituted by chloro- or bromo-allyl groups, $CH_2{=}CXCH_2{-}$, for use as one component of the pairs to be rearranged in admixture, were unsuccessful. The use of such esters would have simplified the problem of determining whether an interchange of groups occurred. If no interchange took place, the rearrangement product derived from the original ester which did not contain halogen would be halogen free. Also, the extent of a possible partial interchange could be determined by quantitative analysis for halogen.

It was consequently necessary to employ for rearrangement in admixture pairs of esters which yielded isomerization products with different boiling points, which could be separated by fractional distillation.

The first mixture rearranged was composed of the ester I and ethyl (1-methyl 1-hexenyl)-allylcyanoacetate, V. If the rearrangement is intramolecular, no interchange of groups should occur, and I should rearrange to III and V to VI.


V

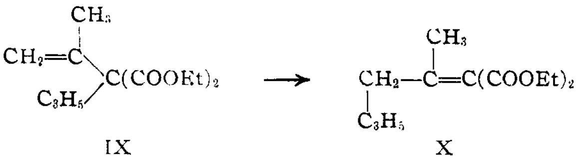
VI

Fractionation of the rearrangement product actually obtained gave low and high boiling fractions which were homogeneous and composed of the pure esters III and VI. This was proved by cleaving the two fractions with concd. aqueous ammonia and identifying the ketones which were formed. An intermediate fraction boiling between the temperatures at which the pure rearrangement products distilled was also analyzed by cleavage with ammonium hydroxide. The cleavage products were the same two ketones which had been obtained from the end fractions. Consequently, the intermediate fraction was simply composed of a mixture of III and VI, which were not completely separated because of the proximity of their boiling points.

For confirmation of these results, a mixture of II and V was rearranged, and the products separated by fractional distillation. They proved to be VII and VI, and the intermediate fraction was composed of a mixture of VII and VI.

Thus only products formed by intramolecular rearrangement were isolated from the mixtures. While the separations were not complete nor the yields of derivatives quantitative, within the limits of this method of investigation the rearrangements are intramolecular. These results confirm the conclusions reached from kinetic studies described in the preceding paper.

During the search for compounds suitable for rearrangement in mixtures, one additional ester, ethyl isopropenyl-allylmalonate, IX, was prepared[10] and rearranged by heating to ethyl (1-methyl-4-pentenylidene)-malonate, X.


IX

X

Experimental Part[11]

Ethyl Isopropenyl-crotylmalonate (I).—The sodium enolate prepared from ethyl isopropylidenemalonate (100 g.) and sodamide was alkylated in toluene suspension with crotyl bromide[12] (86.4 g.) by the general procedure previously described.[6] The reaction mixture was practically neutral after refluxing for one and one-half hours. The mixture was cooled, washed with water, and distilled. The crude product (102 g., b. p. 105–145° (2 mm.)) was shaken with 400 cc. of concd. aqueous ammonia for twenty-four hours and redistilled through a Widmer column. The yield of I was 77.2 g. (61%); b. p. 98–100° (2 mm.); $n^{25}\text{D}$ 1.4536; d^{25}_{25} 0.9938; M_D calcd. 69.24, found 69.41.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.09; H, 8.72. Found: C, 66.28; H, 8.54.

Proof of Structure of I.—The ester I (10 g.) in 50 cc. of alcohol was hydrogenated in the presence of 1 g. of palladinized charcoal.[13] Two molar equivalents of hydrogen was absorbed in three hours. Distillation gave 8.7 g. of ethyl isopropyl-butylmalonate, b. p. 143–145° (23 mm.), $n^{25}\text{D}$ 1.4323. Condensation of this ester with urea in the usual manner[14] produced 5-butyl-5-isopropylbarbituric acid, m. p. and mixed m. p. with a known sample 154–155°.[15]

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[10] This ester had been prepared previously and is described in ref. 6. Its rearrangement was not observed in the previous study, because the temperature at which it was distilled is below the temperature at which it rearranges.

[11] All melting and boiling points are uncorrected.

[12] The crotyl bromide employed in the alkylations had b. p. 46–47° (88 mm.), $n^{25}\text{D}$ 1.4775. It consequently contained 10% of its allylic isomer, methylvinylcarbinyl bromide; *cf.* Winstein and Young, THIS JOURNAL, **58**, 104 (1936). It was not considered necessary to use crotyl bromide completely free from methylvinylcarbinyl bromide, because the two halides would probably undergo rapid interconversion under conditions pertaining in the alkylation. Moreover, the enolates of branched chain monoalkyl malonic and cyanoacetic esters react much more rapidly with primary than with secondary bromides, so that their reaction with a mixture of crotyl and methylvinylcarbinyl bromides would be expected to yield principally crotyl rather than methylvinylcarbinyl substituted derivatives.

[13] Hartung, *ibid.*, **50**, 3372 (1928).

[14] Fischer and Dilthey, *Ann.*, **335**, 338 (1904).

[15] Cope, Hartung, Hancock and Crossley, THIS JOURNAL, **62**, 1200 (1940).

Ethyl (1,3-Dimethyl-4-pentenylidene)-malonate (III).—Compound I (25.4 g.) was refluxed at 185° in vacuum for two hours and distilled through a Widmer column. This treatment resulted in complete rearrangement of I to III, for the product had the same index of refraction as a sample of III prepared by successively heating and distilling I until there was no change in refractive index, in the manner described in the preceding paper. The yield of III was 22.7 g., b. p. 161–163° (27 mm.); n^{25}_{D} 1.4590; d^{25}_{25} 0.9901; M_{D} calcd. 69.24, found 70.32, exaltation 1.08.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.09; H, 8.72. Found: C, 65.91; H, 8.70.

Proof of Structure of III.—III (22.7 g.) was shaken with 225 cc. of concd. aqueous ammonia for ten days. The ketone layer was separated, the aqueous layer extracted with ether, and the extract and ketone dried over potassium carbonate. On distillation 4.4 g. (44%) of 4-methyl-5-hexen-2-one (IV) was obtained, b. p. 137–138°; n^{25}_{D} 1.4193; d^{25}_{25} 0.8297; M_{D} calcd. 34.08, found 34.23.

Anal. Calcd. for $C_7H_{12}O$: C, 74.93; H, 10.70. Found: C, 74.88; H, 10.57.

The semicarbazone of 4-methyl-5-hexen-2-one, prepared in the usual manner and recrystallized from dilute alcohol, melted at 112.5–113.5°.

Anal. Calcd. for $C_8H_{15}ON_3$: N, 24.84. Found: N, 25.10.

The unsaturated ketone IV(2.63 g.) absorbed 100.5% of one molar equivalent of hydrogen in a quantitative reduction carried out in alcohol solution in the presence of palladinized charcoal. The reduction product, b. p. 137–138°, was proved to be 4-methylhexan-2-one (*s*-butylacetone), by preparing its semicarbazone, whose m. p. and mixed m. p. with a known specimen (described below) was 119–120°. If IV had rearranged without inversion the product of the above series of transformations would have been methyl amyl ketone, whose semicarbazone also melts at 119–120°. The mixed m. p. of the semicarbazone of the latter ketone and the derivative of the ketone obtained by reduction was 102–106°.

***s*-Butylacetone.**—Isopropyl *s*-butylacetoacetate (39.3 g.) was refluxed with 315 cc. of 10% potassium hydroxide for sixteen hours. The ketone layer which separated and the ether extract of the aqueous layer were dried over potassium carbonate and distilled, yielding 12 g. (52%) of *s*-butylacetone, b. p. 137–139°, n^{25}_{D} 1.4057. The semicarbazone of this ketone, recrystallized from dilute alcohol, melted at 119–120°, in agreement with one recorded m. p.[16]

Isopropyl *s*-butylacetoacetate was prepared by adding *s*-butyl bromide (37.7 g.) at 60° to the sodium enolate obtained from isopropyl acetoacetate (36 g.) and a solution of 5.75 g. of sodium in 250 cc. of dry isopropyl alcohol. The mixture was refluxed for nine hours, cooled and added to two liters of water containing enough hydrochloric acid to make the solution slightly acid. The ester was extracted with benzene and distilled through a Widmer column. A large portion (24.2 g.) of the isopropyl acetoacetate was recovered while the yield of isopropyl *s*-butylacetoacetate was 9.1 g. (18%), b. p. 98–99° (11 mm.); n^{25}_{D} 1.4254; d^{25}_{25} 0.9351; M_{D} calcd. 54.68, found 54.77.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.95; H, 10.07. Found: C, 65.88; H, 10.01.

Ethyl (1-Methyl-propenyl)-crotylcyanoacetate (II).—The sodium enolate prepared from ethyl (1-methylpropylidene)-cyanoacetate (41.8 g.) and a solution of 5.75 g. of sodium in 200 cc. of absolute alcohol was alkylated with crotyl bromide[12] (43.2 g.) by the general procedure described before.[7] The mixture was neutral after refluxing for five minutes. The crude product (32.7 g., b. p. 95–150° (2 mm.)) was purified by shaking with 100 cc. of 20% sodium bisulfite solution for twelve hours and redistilled through a Widmer column. The yield of II was 16.1 g. (30%); b. p. 109–111° (3 mm.); n^{25}_{D} 1.4637; d^{25}_{25} 0.9668; M_{D} calcd. 62.79, found 63.26.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.31. Found: N, 6.28

Proof of Structure II.—When II (10 g.) in 50 cc. of alcohol was reduced in the presence of 1 g. of palladinized charcoal, one equivalent of hydrogen was absorbed in one and one-half hours, after which the reduction proceeded very slowly. After twenty hours the catalyst was filtered and the product distilled. An ester (7.9 g., b. p. 151–153° (21 mm.), n^{25}_{D} 1.4453) was obtained which was evidently a mixture formed by incomplete reduction of II. When this ester (6.7 g.) was condensed with urea in the usual manner, the product (3.8 g., m. p. 132–142°) was a mixture which was purified by several recrystallizations from dilute alcohol and precipitation from sodium hydroxide solution by carbon dioxide. The product isolated was 5-*n*-butyl 5-(1-methyl-propenyl)-barbituric acid (1.6 g.), m. p. 165–165.5°; mixed m. p. with a known sample[17] 166–167°. The isolation of this unsaturated barbituric acid establishes the carbon skeleton in II; for confirmation it was hydrogenated quantitatively (100.0% hydrogen absorption) to 5-*n*-butyl 5-*s*-butylbarbituric acid (0.3 g. from the reduction of 0.4 g.), m. p. 132–133.5°; mixed m. p. with a known sample 131–133.5°.

Anal. Calcd. for $C_{12}H_{20}O_3N_2$: N, 11.66. Found: N, 11.55.

Ethyl (1,2,3-Trimethyl-4-pentenylidene)-cyanoacetate (VII).—II (20.1 g.) was refluxed at 180° in vacuum for five and one-half hours and distilled through a Widmer column. Subsequent rearrangements showed that a much shorter period of heating would have sufficed. The yield of VII was 16.1 g., b. p. 157–160° (23 mm.); n^{25}_{D} 1.4741; d^{25}_{25} 0.9692; M_{D} calcd. 62.79, found 64.32, exaltation 1.53.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.31. Found: N, 6.19.

Proof of Structure of VII.—VII (16.2 g.) was shaken overnight with 160 cc. of concd. aqueous ammonia. The ketone which separated was combined with an ether extract of the aqueous layer, dried over potassium carbonate and distilled. 3,4-Dimethyl-5-hexen-2-one (VIII) (5.2 g., 56%) was obtained, b. p. 151–154°; n^{25}_{D} 1.4267; d^{25}_{25} 0.8360; M_{D} calcd. 38.70, found 38.82.

Anal. Calcd. for $C_8H_{14}O$: C, 76.12; H, 11.19. Found: C, 76.27; H, 11.33.

The semicarbazone of 3,4-dimethyl-5-hexen-2-one, after several recrystallizations from dilute alcohol, melted at 89–90°.

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[16] Davies, Dixon and Jones, *J. Chem. Soc.*, 471 (1930). Rhinesmith, THIS JOURNAL, **58**, 596 (1936), gives the m. p. as 127–128°.

[17] Cope and Hancock, *ibid.*, **61**, 353 (1939).

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.94. Found: N, 22.87.

In a quantitative reduction 2.70 g. of the unsaturated ketone VIII absorbed 100.9% of one molar equivalent of hydrogen. On distillation 1.2 g. of 3,4-dimethylhexan-2-one (*unsym-s*-butylmethylacetone) was obtained, b. p. 153–154°. The ketone was converted into its semicarbazone for identification. After recrystallization from dilute alcohol the semicarbazone melted at 136.5–137.5°; mixed m. p. with a known sample 135.5–137°.

Anal. Calcd. for $C_9H_{19}ON_3$: N, 22.69. Found: N, 22.55.

The known 3,4-dimethylhexan-2-one semicarbazone used in the above comparison was prepared from a sample of the ketone obtained by the hydrolysis of ethyl *s*-butylmethylacetoacetate.[18] This semicarbazone has been reported as melting at 119°[19] and 124–126°[20]; because of the discrepancy our sample of m. p. 136.5–137.5° was analyzed.

Rearrangement of Mixtures. A. Simultaneous Rearrangement of I and V.[21]—Preliminary rate measurements by the refractive index method outlined in the preceding paper showed that I rearranged approximately one-half as fast as V at 193.1 ± 0.5°. Consequently, when a mixture of the two esters is rearranged, there would be an opportunity for interchange of groups if the rearrangement were intermolecular.

A mixture of 30 g. of I and 30 g. of V was rearranged by refluxing at 175 to 180° in vacuum for two hours. The resulting mixture was fractionated twice through a Widmer column, and separated into the following fractions: (a) 19.6 g., b. p. 95–100° (2 mm.), $n^{25}\mathrm{D}$ 1.4590 (these properties correspond closely to those of pure III); (b) 15.2 g., b. p. 103–113° (2 mm.), $n^{25}\mathrm{D}$ 1.4665 (the intermediate fraction); (c) 16.2 g., b. p. 113–115° (2 mm.), $n^{25}\mathrm{D}$ 1.4759 (corresponding to the properties of pure VI[21]). Fraction (a) was cleaved by shaking with 200 cc. of concd. aqueous ammonia for ten days. The ketone formed was extracted and distilled; yield 2 g., b. p. 137–141°; $n^{25}\mathrm{D}$ 1.4193; m. p. of the semicarbazone 112–113°, not depressed when mixed with the semicarbazone of IV. Fraction (c) was cleaved by shaking with concd. ammonium hydroxide for forty-eight hours. The ketone obtained (4 g.) had b. p. 190–193°; $n^{25}\mathrm{D}$ 1.4329; m. p. of the 2,4-dinitrophenylhydrazone 48–49°, not depressed when mixed with the dinitrophenylhydrazone of *unsym-n*-butyl allylacetone.[4] Fraction (b) was shaken with 160 cc. of concd. aqueous ammonia for nine days. The ketones were extracted and separated by distillation from a small modified Claisen flask. The lower boiling ketone (1.6 g., b. p. 137–145°, $n^{25}\mathrm{D}$ 1.4194) was proved to be IV by reduction and preparation of the semicarbazone of the reduction product (*s*-butylacetone). The higher boiling fraction (2 g., b. p. 190–200°; $n^{25}\mathrm{D}$ 1.4334) was identified as *unsym-n*-butylallylacetone by preparation of the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 47.5–49°.

B. Simultaneous Rearrangement of II and V.—Preliminary measurements showed that II and V rearranged at the same rate at 193.1 ± 0.5°, within experimental error.

A mixture of 22 g. of II and 22 g. of V was rearranged by refluxing at 185–190° in vacuum for two hours. The product was fractionated twice through a Widmer column. The following fractions were separated: (a) 12.9 g., b. p. 105–107° (3 mm.), $n^{25}\mathrm{D}$ 1.4740 (properties corresponding to VII); (b) 13.4 g., b. p. 104–117° (2 mm.), $n^{25}\mathrm{D}$ 1.4754 (intermediate); (c) 9.8 g., b. p. 117–121° (2 mm.), $n^{25}\mathrm{D}$ 1.4757 (properties corresponding to VI). Fraction (a) was cleaved by shaking with concd. aqueous ammonia for twenty-four hours to VIII (3 g., b. p. 153–158°, $n^{25}\mathrm{D}$ 1.4264), identified as the semicarbazone, m. p. and mixed m. p. 88.5–90°. Fraction (c) was cleaved in the same way to *unsym-n*-butylallylacetone (2.1 g., b. p. 188–192°, $n^{25}\mathrm{D}$ 1.4332), identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 47.5–49°. The intermediate fraction (c) was also cleaved in the same way to a mixture of VIII (1.5 g.) and *unsym-n*-butylallylacetone (1.2 g.).

Ethyl (1-Methyl-4-pentenylidene-malonate (X).—Ethyl isopropenylallylmalonate (IX)[10] (24 g.) was refluxed at 180–190° in vacuum for a total of fourteen hours and distilled. The yield of X was 14 g. (considerable material was lost because the product was distilled three times before rearrangement was found to be complete), b. p. 134–136° (10 mm.); $n^{25}\mathrm{D}$ 1.4610; $d^{25}{}_{25}$ 1.0033; $M\mathrm{D}$ calcd. 64.62, found 65.88, exaltation 1.26.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.96; H, 8.39. Found: C, 64.86; H, 8.25.

X (6 g.) was shaken with 50 cc. of concd. aqueous ammonia for ten days. Extraction with ether and distillation gave 1.1 g. of allylacetone, b. p. 126°, which was identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. with a known sample 107.5–109°.[22]

Other Alkylations Attempted.—The alkylation of sodium enolates prepared from ethyl isopropylidene malonate and ethyl (1-methyl propylidene) cyanoacetate with cinnamyl bromide, 2,3-dichloropropene and 2,3-dibromopropene gave very small amounts of products which did not have constant boiling points or refractive indexes. In each case the greater part of the product decomposed during distillation, even at 1×10^{-5} mm. Alkylation of sodium enolates prepared from ethyl (1-methyl-propylidene)-cyanoacetate and ethyl (1-methylhexylidene)-cyanoacetate with methallyl chloride gave 20–35% yields of alkylated esters, which rearranged partially on distillation, even at 1×10^{-5} mm., and consequently were not investigated further.

Summary

Ethyl isopropenylcrotylmalonate and ethyl (1-methylpropenyl)-crotylcyanoacetate have been prepared and isomerized by heating. In each case the rearrangement proceeded with *inversion* of the crotyl group.

Evidence that the rearrangement of allyl groups in three-carbon systems is intramolecular was obtained by rearranging mixtures of two

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[18] We are indebted to Miss Dorothea Heyl for this preparation.

[19] Colonge, *Bull. soc. chim.*, [4] **49**, 447 (1931); *ibid.*, [5] **2**, 758 (1935).

[20] Powell and Secoy, THIS JOURNAL, **53**, 768 (1931).

[21] This compound and its rearrangement product, VI, are described in ref. 4 and designated there by formulas V and VI.

[22] Allen, THIS JOURNAL, **52**, 2958 (1930), gives the m. p. as 104°.

esters, one of which was substituted by a crotyl and the other by an allyl group. No interchange of the migrating groups occurred.

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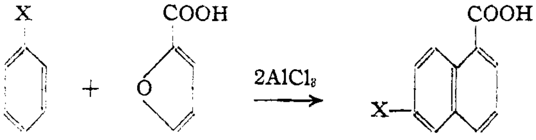
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of Furoic Acid with Aromatic Compounds*

BY CHARLES C. PRICE, E. C. CHAPIN, ARTHUR GOLDMAN, EDWIN KREBS AND H. M. SHAFER

In a search for a synthesis of certain naphthalene derivatives of known structure, the possibility of the application of the reaction of aromatic compounds with furoic acid in the presence of aluminum chloride has been investigated. Gilman, McCorkle and Calloway[1] have found that the acid obtained by King[2] from such a reaction of furoic acid with benzene was not phenyldihydrofuroic acid, but rather α-naphthoic acid, and McCorkle and Turck[3] have reported that toluene, anisole and chlorobenzene reacted similarly yielding the corresponding 6-substituted-1-naphthoic acids.

We have also isolated these products and have confirmed their structure, but in every case the yield of pure crystalline acid obtained was small (10–20%).



I

(10–20%)

(X = H, CH_3, OCH_3 or Cl)

The low yield of naphthoic acid has been accounted for, however, since we have found the major product of the reaction to be a mixture of higher molecular weight acids of complex structure, formed by the condensation of two or three molecules of the aromatic compound with one of furoic acid. The various naphthoic acids could be separated from these larger acids by extraction of the particular reaction mixture, after hydrolysis, with aqueous sodium bicarbonate. The high molecular weight acids were not extracted to any appreciable extent by this procedure although they were readily extracted by dilute sodium hydroxide.

From the reaction with benzene, the crude acid obtained from the bicarbonate extract contained about 30% α-naphthoic acid, the remainder consisting of a small amount (10–15%) of an amorphous acid and unreacted furoic acid. The α-naphthoic acid could be obtained from this mixture by recrystallization from toluene, or more satisfactorily by treatment with barium hydroxide. Barium α-naphthoate (and barium furoate) dissolved in hot water while the higher molecular weight acid formed an insoluble barium salt. The α-naphthoic acid (I, X = H) was identified by melting point and mixed melting point, by its neutral equivalent and by conversion to the anilide and to 5-bromo-1-naphthoic acid.

After removal of the naphthoic acid with bicarbonate, the high molecular weight acids were obtained readily by extraction with 2 to 5% sodium hydroxide. Acidification of such extracts yielded an amorphous powder which resisted all attempts at crystallization. On the basis of its analysis and neutral equivalent this material was a mixture which consisted principally of an acid formed by the condensation of three molecules of benzene with one of furoic acid, accompanied by the elimination of one molecule of water, contaminated with a similar product formed from two molecules of benzene and one of furoic acid. Decarboxylation of this mixture with copper chromite in quinoline gave a neutral oil in 50% yield which was readily dehydrogenated with sulfur to yield 22% of pure crystalline 1,4-diphenylnaphthalene, identified by analysis as well as by its melting point alone and admixed with an authentic sample.[4] The isolation of this hydrocarbon indicates that the product of the condensation of three molecules of benzene with one of furoic acid is 1,4-diphenyl-1,2,3,4-tetrahydro-1-naphthoic acid (III). This compound differs structurally from the α-naphthoic acid formed

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[1] Gilman, McCorkle and Calloway, THIS JOURNAL, **56**, 745 (1934); see also Calloway, *Chem. Rev.*, **17**, 343 (1935).

[2] King, THIS JOURNAL, **49**, 565 (1927).

[3] McCorkle and Turck, *Proc. Iowa Acad. Sci.*, **43**, 205 (1936).

[4] The authors are indebted to Dr. C. F. H. Allen for the authentic sample of 1,4-diphenylnaphthalene (Allen and Gilman, THIS JOURNAL, **58**, 937 (1936)).