

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY, LEXINGTON, KY.]

The Reaction of 3-Phenyl-1-butene-3-¹⁴C with Formic Acid^{1,2}

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Extensive isotope-position rearrangement attends the addition of formic acid to 3-phenyl-1-butene-3-¹⁴C. This result suggests that 3-phenyl-2-butyl formate product is formed from at least two structurally distinct intermediates, one of which is *phenonium* ion. Formic acid reacts with 1-octene about 9 times faster than with 3-phenyl-1-butene. This result shows that *phenonium* ion probably is not produced from 3-phenyl-1-butene in a rate-determining step. It appears that a relatively slow step occurs early in these reactions.

3-Phenyl-1-butene (I) reacted with hot formic acid without catalyst to give a mixture of diastereoisomeric 3-phenyl-2-butyl formates (III) and 2-phenyl-2-butene (II). The course of the reaction was followed by means of gas chromatography, and the results obtained in two runs at 80° in 99.7% formic acid are summarized in Table I.

TABLE I
THE REACTION OF 3-PHENYL-1-BUTENE WITH 99.7% FORMIC ACID^a AT 80.2 ± 0.1°

Time, hr.	[I] ^b	[<i>cis</i> -II] ^b	[III] ^b	k, ^c hr. ⁻¹
0.0	0.248			
6.6	.115	0.010	0.121	0.117
10.8	.061	.011	.174	.130
24.6	.012	.008	.220	.123
30.3	.008	.007	.228	.113
			Av. 0.121	
0.0	0.266			
6.6	.131	0.010	0.122	0.108
10.8	.076	.011	.174	.116
24.7	.016	.008	.236	.114
30.1	.007	.006	.248	.121
			Av. 0.115	

^a Freezing point 7.8°. ^b Estimated from areas under elution peaks in gas chromatography as described in the Experimental section. ^c Rate constant for disappearance of I.

The ratio of 3-phenyl-2-butyl formate (III) to *cis*-2-phenyl-2-butene (*cis*-II) was approximately 12 after one reaction half-life, but the relative amount of conjugated olefin decreased slowly during long reaction time owing to conversion of II into high-boiling material. A control experiment showed that *trans*-II is equilibrated with *cis*-II and 2-phenyl-1-butene under the reaction conditions. The ratio³ *cis*-II:*trans*-II:2-phenyl-1-butene in formic acid at 80° was approximately 20:4:1 after 35 minutes and the ratio did not change thereafter, but the amount of conjugated phenyl-butenes decreased steadily as they were converted into a dimeric hydrocarbon of unknown structure. The retention time of *trans*-II in gas chromatography was identical with that of I; consequently *trans*-II was not detected among the products of reaction of I with formic acid.

3-Phenyl-1-butene-3-¹⁴C (I-3-¹⁴C) was prepared by pyrolysis of 3-phenyl-1-butyl-3-¹⁴C acetate at

(1) Presented at the Organic Division, A.C.S. Meeting, Cleveland, Ohio, April, 1960, abstracts p. 51-O.

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(3) Estimated from areas under elution peaks in gas chromatography.

475 ± 10°. A small amount (*ca.* 3%) of ¹⁴C-activity was lost from C-3 during the elimination of acetic acid from the acetate,⁴ but this does not seriously complicate the interpretation of results obtained in the reaction of I-3-¹⁴C with formic acid.

3-Phenyl-1-butene-3-¹⁴C (I-3-¹⁴C) was allowed to react with 99.7% formic acid for a period of 6.5 hours at 80°. The crude product mixture was examined by gas chromatography, and I-X-¹⁴C and 3-phenyl-2-butyl-X-¹⁴C formate (III-X-¹⁴C) were isolated by fractional distillation (*cf.* Table II).

TABLE II

THE PRODUCTS OF REACTION OF 3-PHENYL-1-BUTENE-3-¹⁴C^a WITH 99.7% FORMIC ACID AT 80.2 ± 0.1° FOR 6.50 HOURS

Compound	Yield, b %
3-Phenyl-1-butene-X- ¹⁴ C (I)	43 (36) ^c
<i>cis</i> -2-Phenyl-2-butene (II)	4
3-Phenyl-2-butyl-X- ¹⁴ C formate (III)	53 (48) ^c

^a Initial concentration 0.123 M. ^b Estimated from areas under elution peaks in gas chromatography. ^c Isolated by fractional distillation.

Compound I-X-¹⁴C was identified by its boiling point, infrared spectrum, and retention time in gas chromatography; III-X-¹⁴C was converted by means of lithium aluminum hydride in ether into a mixture of diastereoisomeric 3-phenyl-2-butanol-3-¹⁴C (IV), which had an infrared spectrum and two elution peaks in gas chromatography corresponding to those of the diastereoisomeric mixture of IV obtained by reaction of hydratropaldehyde with methyl Grignard reagent.⁵ The product IV and recovered starting material I were each oxidized to benzoic acid for radioassay of C-3. These and related ¹⁴C-activity measurements are summarized in Table III.

An experiment was designed to test the possibility that all or part of the extensive isotope-position rearrangement that occurred in the production of 3-phenyl-2-butyl formate (III) from 3-phenyl-1-butene-3-¹⁴C (I) (Table III) might have occurred after formation of the ester. The work of Cram on the solvolysis of 3-phenyl-2-butyl derivatives^{5,6}

(4) Isotope-position rearrangement did not occur in the acetate prior to elimination of acetic acid (*cf.* Table III). Passing the labeled olefin through the heated chamber with acetic acid did not cause further loss of ¹⁴C-activity from C-3. Gas chromatography did not reveal a sufficient amount of impurities in the olefin samples to account for the low activities of the benzoic acid fragments. Pyrolysis of 3-phenyl-1-butyl acetate at 500 ± 10° resulted, at most, in only a slight increase in the amount of ¹⁴C-activity lost from C-3. Independent measurements by New England Nuclear Assay Corporation, Boston, Mass., indicated 4 ± 2% loss of ¹⁴C-activity from C-3 in pyrolysis of the acetate at both temperatures. We are greatly indebted to Dr. Robert E. Leary for his help with this part of the experimental work.

(5) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

(6) D. J. Cram, *ibid.*, **74**, 2129 (1952).

TABLE III
¹⁴C-ACTIVITY MEASUREMENTS ON THE 3-PHENYL-1-BUTENE-
 3-¹⁴C-FORMIC ACID REACTION PRODUCTS

Compound	Counts/ min. ^a	Rearrangement, %
3-Phenyl-1-butanol-3- ¹⁴ C	1520 ± 19 ^c	
Benzoic acid fragment from: 3-phenyl-1-butene-3- ¹⁴ C (I)	1487 ± 20	2.4 ± 1.5 (5 ± 2) ^d
recovered acetate ^e	1523 ± 11	0
3-phenyl-2-butanol-X- ¹⁴ C (IV)	862 ± 21	43.3 ± 1.4 ^f (46 ± 2) ^{d, g}
recov. 3-phenyl-1-butene (I)	1483 ± 15	2.5 ± 1.2 (4 ± 2) ^d

^a Mean activity of five or more plates of barium carbonate, corrected for background (12 to 16 counts/min.), coincidence and sample thickness, together with the probable error, 0.674σ. Measurements were made with a gas-flow counter of the Sugarman type, operated as a Geiger counter. ^b Percentage loss of ¹⁴C-activity from C-3, together with the probable error as defined by F. Daniels, *et al.*, "Experimental Physical Chemistry," fifth edition, McGraw-Hill Book Co., Inc., 1956, p. 328. ^c The corrected activity was multiplied by 11/7 to adjust for relative carbon content. ^d Result obtained from an independent but very comparable experiment. The ¹⁴C-activity measurements were made on solutions of the compounds named using an internal scintillator by New England Nuclear Assay Corp., Boston, Mass. ^e From the olefin-forming pyrolysis at 475°. ^f Contained 92% *erythro* isomer. ^g Contained 60% of the *erythro* isomer.

suggested that an examination of the optical stability of optically active *threo*-III⁷ in hot formic acid would provide the desired information.

It was found that 3-phenyl-2-butanol (IV) in formic acid at 80° for one-half hour was converted quantitatively into III, and it seemed feasible to examine the optical stability of optically active *threo*-III in formic acid by employing the optically active carbinol. The results of this experiment, which are summarized in Table IV, indicate that

TABLE IV
 THE RACEMIZATION OF (-)-*threo*-3-PHENYL-2-BUTANOL^a
 IN 99.7% FORMIC ACID AT 80.2 ± 0.1°

Time, hr.	Rotation ^b	k, hr. ⁻¹
0.00	-3.50 ± 0.02°	
2.00	-2.80 ± .02	0.112
8.00	-1.56 ± .02	0.101
120	-0.03 ± .02	
		Av. 0.106

^a Concentration 0.075 M. ^b Recovered carbinol, 1.00 ml., diluted to 12.5 ml. with cyclohexane, 12 dm.

the carbinol is esterified rapidly in formic acid, and that the error introduced by starting with optically active carbinol rather than with ester is small. Each of the ester samples obtained in this experiment was converted by means of lithium aluminum hydride in ether into the corresponding carbinol prior to measurement of optical rotation. The recovered carbinol gave, in each case, a single elution peak in gas chromatography, corresponding in retention time to that of authentic *threo*-IV.

The reaction of 1-octene with formic acid was examined briefly so that the reactivity of a simple monosubstituted olefin could be compared with that of 3-phenyl-1-butene (I); the results obtained in a small-scale preparative run at 80° are sum-

(7) The diastereoisomeric 3-phenyl-2-butanol designated as I by Cram is designated *threo*-3-phenyl-2-butanol in this paper. See ref. 5 and 6, and see W. G. Dauben and K. S. Pitzer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 10.

marized in Table V. 1-Octene was found to react approximately nine times faster than I with formic acid at this temperature.

TABLE V
 THE REACTION OF 1-OCTENE^a WITH 99.5% FORMIC ACID AT
 80.2 ± 0.1° FOR 45 MINUTES

Compound	Yield, % ^b
1-Octene	45 (41) ^c
2-Octyl formate	55 (51) ^c

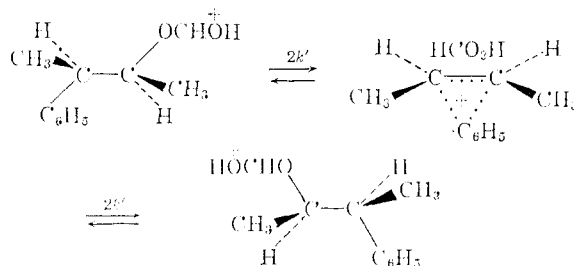
^a Initial concentration 0.40 M. ^b Estimated from areas under elution peaks in gas chromatography. ^c Isolated by distillation.

In another experiment, the reaction of 1-octene with formic acid was allowed to proceed to 89% conversion of the olefin into 2-octyl formate. The reaction was very clean; neither 2-octene nor 3-octyl formate could be detected in the crude product mixture by means of gas chromatography.

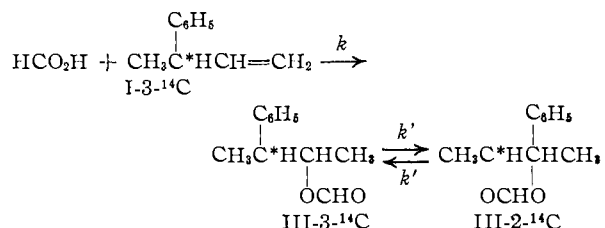
Discussion

The data of Table III show that extensive isotope-position rearrangement accompanied the addition of formic acid to 3-phenyl-1-butene-3-¹⁴C. It is clear that the observed rearrangement did not occur in the olefin prior to addition of formic acid, since recovered olefin showed no loss of ¹⁴C-activity from C-3.

The racemization of (-)-*threo*-3-phenyl-2-butyl formate ((-)-*threo*-III) that was observed to occur in hot formic acid (Table IV) indicates that some loss of ¹⁴C-activity from C-3 of III-3-¹⁴C occurred after the ester was formed. A plausible interpretation of the racemization is that the ester underwent slow ionization in formic acid to produce symmetrical *phenonium* ion⁵ or, possibly, *phenonium*



formate ion-pair.^{6,8} Such a process would result in transfer of ¹⁴C-activity from C-3 to C-2 of the labeled ester, and, if 2k' is the first-order rate constant for racemization, k' is the appropriate rate constant for transfer of ¹⁴C-activity. We may use, to a reasonable approximation for present purposes, the same rate constant, k', for isotope transfer in both *erythro*-III and *threo*-III.



(8) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952).

The amount of isotope-position rearrangement to be expected if the rearrangement were to have occurred only after the ester was produced from 3-phenyl-1-butene-3-¹⁴C (I-3-¹⁴C) can be estimated in a straightforward manner. If a_0 is the initial concentration of I-3-¹⁴C, and b and c are the concentrations at time t of III-3-¹⁴C and III-2-¹⁴C respectively, then

$$dc/dt = k'a_0(1 - e^{-kt}) - 2k'c$$

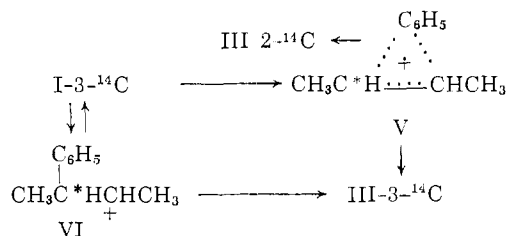
and⁹

$$c/a_0 = 1/2 - k'e^{-kt}/(2k' - k) + ke^{-2kt}/2(2k' - k)$$

For $t = 6.50$ hr., $k = 0.110 \pm 0.007$ hr.⁻¹,¹⁰ and $k' = 0.053 \pm 0.003$ hr.⁻¹ (Table IV), we find $c/a_0 = 0.076 \pm 0.014$. Since $(b + c) = 0.53a_0$ at $t = 6.50$ hr. (Table II), we obtain for $c/(b + c)$, the fraction of 3-phenyl-2-butyl formate that would be rearranged, the value 0.144 ± 0.026 . The fractional loss of ¹⁴C label from C-3 that actually occurred in the addition of formic acid to I-3-¹⁴C was 0.433 (Table III), and it is clear that most of the observed isotope-position rearrangement occurred during the addition of formic acid to the olefin.

Since extensive isotope-position rearrangement accompanies the addition of formic acid to 3-phenyl-1-butene-3-¹⁴C, the further loss of ¹⁴C-activity from C-3 of the ester product during the 6.5 hours reaction time is small. In the present reaction it appears that approximately 40% isotope-position rearrangement accompanied the addition of formic acid,¹¹ and that the loss of ¹⁴C-activity from C-3 was increased to 43% by the ionization of ester to *phenonium* ion.

A possible interpretation of the isotope-position rearrangement that attends the addition of formic acid to 3-phenyl-1-butene-3-¹⁴C is that four-fifths of the reaction proceeds by a path involving direct production of the *phenonium* ion V from the olefin and the remaining one-fifth proceeds by an independent path involving the "open" secondary carbonium ion VI. According to this interpreta-



tion, V and VI are produced in relatively slow steps from the olefin, and the path involving *phenonium* ion is favored by participation of the neighboring phenyl group with the reaction center.¹² This

(9) We are indebted to Mr. Achmad Amiruddin for the general solution of this rate expression.

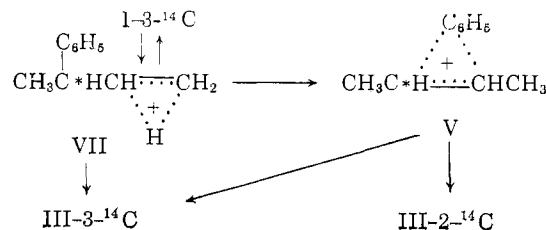
(10) The average value for the rate constant for the disappearance of I, obtained from the data of Tables I and II, is 0.122 hr.⁻¹. The rate constant for ester formation is about 10% smaller than this.

(11) The error introduced into this estimate of percentage rearrangement by the slight loss of ¹⁴C-activity from C-3 during the preparation of I-3-¹⁴C is almost negligible. If the lost activity is located at C-2 of the labeled olefin, the error is about 0.5 percentage unit.

(12) *threo*-3-Phenyl-2-butyl *p*-toluenesulfonate ionizes approximately 5 times faster than 2-butyl *p*-toluenesulfonate in formic acid at 25° (ref. 8). In the present reaction scheme both reaction paths are subject to the unfavorable inductive effect of the phenyl group

view leads to the prediction that 3-phenyl-1-butene (I), in spite of an unfavorable inductive effect by the phenyl group, should react with formic acid somewhat faster than simple monosubstituted olefins in which neighboring group participation is not favorable. Since 1-octene was found to react about 9 times faster than I with formic acid at 80°, it does not seem probable that the *phenonium* ion was formed in a relatively slow step of the addition of formic acid to I. The relative reactivities of I and 1-octene make it appear likely that a slow step occurs early in these reactions.

Another possible interpretation of the present results is that a hydrogen-bridged carbonium ion (VII) is formed from 3-phenyl-1-butene (I) in a relatively slow step. The ion VII may undergo rearrangement to *phenonium* ion V; it may react with formic acid to give ester without isotope-position rearrangement; or it may lose a proton to regenerate I. The approximately 40% isotope-position rearrangement that attended the formation of III from I-3-¹⁴C suggests that the rearrangement of VII to V is about four times as fast as the reaction of VII with formic acid to form III-3-¹⁴C. This interpretation of the present results is, in some of its essential features, like



the one offered for the course of the deamination of 3-phenyl-1-butylamine-3-¹⁴C in acetic acid.¹³

Hydrogen-bridged carbonium ions analogous to VII have been invoked to rationalize stereospecificity observed in the addition of formic acid to 4-*t*-butylcyclohexene,¹⁴ in the addition of hydrogen bromide to 1,2-dimethylcyclohexene,^{15,16} and in the addition of hydrogen chloride to 1,2-dimethylcyclopentene.¹⁶

The slower addition of formic acid to 3-phenyl-1-butene (I) relative to 1-octene may be attributed largely to an inductive effect of the phenyl group at C-3 of I. Alternately, we may regard the entire α -methylbenzyl group of I as "electronegative."^{17,18} From either point of view, the π -electron density of the double bond in I is decreased by inductive

at C-3, and reaction through intermediate V might be expected to be about 50 times faster than reaction by the alternate path through VI. The factor of 4 indicated by the activity measurements of Table III seems to be somewhat too small to offer strong support to the proposed reaction scheme. Since solvolytic displacement in formic acid tends toward the LIM category (S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951)) a comparison between results of solvolysis and formic acid additions seems justified. However, some uncertainties are involved, especially in connection with possible unknown steric factors in the addition of formic acid to olefins.

(13) A. W. Fort and R. E. Leary, *J. Am. Chem. Soc.*, **82**, 2494 (1960).

(14) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(15) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).

(16) (a) C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960); (b) G. S. Hammond and C. H. Collins, *J. Am. Chem. Soc.*, **82**, 4323 (1960).

(17) M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

(18) A. W. Fort and J. D. Roberts, *ibid.*, **78**, 581 (1956).

withdrawal of electrons. Accordingly, the π -electrons of I are less readily available than those of 1-octene for reaction with an electrophilic species such as a proton. Allylic halogen exerts a similar but larger effect on the rate of addition of bromine to monosubstituted olefins.¹⁹

Acknowledgment.—We are indebted to Dr. William D. Ehmann of this department for helpful discussions in connection with our ¹⁴C-activity measurement.

Experimental

Microanalyses are by Drs. Weiler and Strauss, Oxford, England. Melting points and boiling points are uncorrected. Freezing points of formic acid samples were determined with a thermometer calibrated by the National Bureau of Standards.

Formic Acid.—Commercial 98+^o% formic acid was purified by distillation, followed by fractional crystallization. Formic acid purity was estimated from the freezing point as described by Bartlett, Dills and Richey.²⁰

3-Phenyl-1-butene-3-¹⁴C (I-3-¹⁴C).—3-Phenylbutenoic-3-¹⁴C acid was prepared as described previously¹³ and reduced to 3-phenyl-1-butanol-3-¹⁴C as described for the inactive carbinol.¹³ 3-Phenyl-1-butyl-3-¹⁴C acetate was prepared in 90% yield by refluxing the carbinol with acetic anhydride in the presence of pyridine, b.p. 95.5° (2.5 mm.), *n*_D²⁰ 1.4912.

Anal. Calcd. for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 75.19; H, 8.36.

A Vycor tube, packed with glass helices and heated to 475 ± 10°, was flushed with argon, and 3-phenyl-1-butyl-3-¹⁴C acetate was passed through the heated tube with a slow stream of argon. The pyrolysis of 81 g. (0.50 mole) of active acetate gave 24 g. (60% based on unrecovered acetate) of I-3-¹⁴C, b.p. 170° (740 mm.). The infrared spectrum of the olefin product was like that reported²¹ for (–)-3-phenyl-1-butene, but gas chromatography revealed the presence of a trace impurity (ca. 1% of the total area under elution peaks). A mixture of 5.0 g. of the active olefin and 5 ml. of glacial acetic acid was passed through the heated tube under the conditions of the acetate pyrolysis. Recovered olefin, 4.1 g., showed in gas chromatography the same trace impurity that was present before the olefin was passed through the heated tube with acetic acid; the infrared spectrum also was unchanged.

Samples of active 3-phenyl-1-butyl acetate recovered from the pyrolysis reaction and of the active olefin, before and after repass through the pyrolysis tube with acetic acid, were each oxidized to benzoic acid with excess potassium permanganate in refluxing 10% sodium hydroxide solution for ¹⁴C-activity measurements.

3-Phenyl-2-butyl Formate (III).—A solution of a diastereoisomeric mixture of 3-phenyl-2-butanol³ (IV) (4.2 g., 0.028 mole) in 200 ml. of formic acid, f.p. 7.2°, was heated at 79.7 ± 0.1° for 0.5 hour. The reaction mixture was cooled, diluted with ether and neutralized with cold dilute sodium carbonate solution. The ether solution was washed with water, dried, and the ether was removed by distillation. Distillation of the residue at reduced pressure gave 4.6 g. (94%) of III, b.p. 101–102° (10 mm.), *n*_D²⁰ 1.4968. The product²² showed no elution peaks in gas chromatography corresponding to those of the starting carbinol.

Anal. Calcd. for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 74.21; H, 7.92.

The Reaction of 3-Phenyl-1-butene (I) with Formic Acid.—Two reactions of I with formic acid, f.p. 7.8°, were carried out in a constant temperature bath at 80.2 ± 0.1°. Portions of the reaction mixtures, removed at intervals by means of a pipet, were emptied into a relatively large volume of cold ether. The ether solution was ex-

tracted several times with cold dilute sodium hydroxide solution, washed with water, dried, the ether was removed by distillation, and the residue was examined by gas chromatography. The mole % composition of the crude product mixture was estimated from areas under elution peaks by comparison with known mixtures of I, 3-phenyl-2-butyl formate (III) and *cis*-2-phenyl-2-butene (II). The estimation of product ratios was simplified by the fact that *threo*-III and *erythro*-III had identical retention times in the column used. Agreement between the two runs was satisfactory for our requirements (*cf.* Table I), but was not close enough to justify correction for gradual loss of II owing to its conversion into high boiling material.

The Reaction of 3-Phenyl-1-butene-3-¹⁴C (I-3-¹⁴C) with Formic Acid.—A solution of 5.71 g. (0.0432 mole) of I-3-¹⁴C in 350 ml. of formic acid, f.p. 7.8°, was heated in a constant temperature bath at 80.2 ± 0.1° for 6.50 hours. The reaction mixture was treated as described above for the preparation of 3-phenyl-2-butyl formate, and the crude undistilled product mixture was examined by gas chromatography. Yields of the products were estimated from areas under elution peaks as described in the preceding section. Distillation through a 75 × 0.8-cm. column fitted with a tantalum spiral gave: 0.1 g. of forerun which was discarded; 1.81 g., b.p. 65–67° (17 mm.), of I-X-¹⁴C, infrared spectrum like that of starting material, except for weak absorption at 12.0–12.3 μ ; 0.47 g., b.p. 67–122° (17 mm.), of an intermediate fraction, infrared spectrum like that of a mixture of *cis*-2-phenyl-2-butene²¹ (II) and diastereoisomeric 3-phenyl-2-butyl formates (III); 3.44 g., b.p. 122° (17 mm.), of III-X-¹⁴C, identified by its infrared spectrum, and by its retention time²² in gas chromatography; 0.36 g. of column holdup, shown by its retention time in gas chromatography to be III-X-¹⁴C; and 0.17 g. of pot residue.

The fraction b.p. 65–67° (17 mm.) had in gas chromatography a retention time corresponding to that of starting material. There were also two small elution peaks, each ca. 1% of the total area, corresponding in retention times to *cis*-2-phenyl-2-butene (II) and an unidentified impurity that was present in the starting olefin. A portion of this fraction was oxidized to benzoic acid with potassium permanganate in refluxing 10% sodium hydroxide solution.

3-Phenyl-2-butyl formate product (III-X-¹⁴C) (3.4 g., 0.019 mole) was converted into carbinol with lithium aluminum hydride in ether. Distillation gave 2.5 g. (87%) of 3-phenyl-2-butanol (IV-X-¹⁴C). The ratio *erythro*-IV-X-¹⁴C: *threo*-IV-X-¹⁴C was estimated by means of gas chromatography to be approximately 3:2. The acid 3-nitrophthalate ester of the carbinol was recrystallized from ether–ethyl acetate, m.p. 154–155° (lit.⁵ m.p. 156–157°). Saponification and distillation gave 0.65 g. (26% based on starting carbinol) of *erythro*-IV-X-¹⁴C, b.p. 116° (20 mm.), containing³ approximately 8% of *threo*-IV-X-¹⁴C. The active carbinol was oxidized to benzoic acid as described above for I-X-¹⁴C.

In another experiment 4.4 g. (0.033 mole) of I-3-¹⁴C in 140 ml. of formic acid,²³ f.p. 8.1°, was heated at 82.2 ± 0.1° for 5.50 hours and the reaction mixture was worked up as described above. The composition of the crude, undistilled product mixture, estimated from areas under elution peaks in gas chromatography, was 38 ± 2% I-X-¹⁴C, 4 ± 1% *cis*-II and 58 ± 2% III-X-¹⁴C.^{22,24} The products were isolated by fractional distillation as before, and the recovered olefin, b.p. 65–67° (17 mm.), and the active ester, b.p. 94° (5 mm.), were each oxidized to benzoic acid without further treatment.

The Reaction of 2-Phenylbutene (II) with Formic Acid.—A dilute solution of *trans*-II²⁵ containing³ approximately 4 mole % of 2-phenyl-1-butene in formic acid, f.p. 7.8°, was heated at 80.2 ± 0.1°, and samples of the reaction mixture were removed from the constant temperature bath after 0.6 hour and 7.1 hours. The samples were cooled, diluted with ether, and neutralized with cold dilute sodium hydroxide solution. The ether solutions were dried and evaporated, and the residues were examined by means of gas chromatography. The ratio³ *cis*-II:*trans*-II:2-phenyl-1-

(19) J. R. Shelton and L.-H. Lee, *J. Org. Chem.*, **25**, 428 (1960).

(20) P. D. Bartlett, C. E. Dills and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **82**, 5414 (1960).

(21) D. J. Cram, *ibid.*, **74**, 2137 (1952).

(22) The diastereoisomeric esters showed identical retention times in gas chromatography with the column packing used in this work.

(23) The purity, estimated from the freezing point, was 99.9%; see ref. 20.

(24) This reaction was approximately twice as fast as the one described above, a result that can be attributed in part to the very high degree of purity of the formic acid used in this run.

(25) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3883 (1949).

butene was approximately 20:4:1 in each case. The concentration of 2-phenylbutene in the reaction mixture had decreased appreciably in the course of 7.1 hours.

A solution of 2.7 g. of *cis*-II²⁵ in 150 ml. of formic acid, f.p. 8.0°, was heated at 79.7 ± 0.1° for 17 hours. The reaction mixture was worked up as before and distilled to give a trace of forerun, which was discarded, and 1.7 g. of product, b.p. 140–142° (0.8 mm.), *n*_D²⁰ 1.5638.

Anal. Calcd. for C₂₀H₂₄: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 90.88; H, 9.14; mol. wt., 235.

The dimeric hydrocarbon gave negative tests for unsaturation with potassium permanganate in acetone and bromine in carbon tetrachloride. The infrared spectrum of this product showed no indication of an olefinic double bond. Redistillation caused no significant changes in either the infrared spectrum or the elementary analysis.

The Racemization of (–)-*threo*-3-Phenyl-2-butanol ((–)-*threo*-IV).—Racemic *threo*-3-phenyl-2-butyl acid phthalate, m.p. 131–132° (lit.⁵ m.p. 130–131°), was resolved by the procedure of Cram.⁵ Saponification of (–)-*threo*-3-phenyl-2-butyl acid phthalate, m.p. 102–103° (lit.⁵ m.p. 101–102°), gave (–)-*threo*-IV, b.p. 107° (12 mm.) (lit.⁵ b.p. 108° (10 mm.)) which had a single elution peak in gas chromatography.

Three samples of (–)-*threo*-IV were heated at 80.2 ± 0.1° in formic acid, f.p. 7.8°. The reaction mixtures were removed from the constant temperature bath at various times, and the ester products were converted into carbinol with lithium aluminum hydride in ether for measurement of

optical rotation. The results are summarized in Table IV. Flash distillation of the product gave, in each case, 80 to 90% recovery of *threo*-IV, which had a single elution peak in gas chromatography, and which had an infrared spectrum like that of the starting material.

The Reaction of 1-Octene with Formic Acid.—A solution of 1-octene (9.00 g., 0.0802 mole) in 200 ml. of formic acid, f.p. 7.5°, was heated at 80.2 ± 0.1° for 45 minutes. The reaction mixture was neutralized with cold 10% sodium hydroxide solution and extracted with ether. The ether solution was washed with water, dried, and evaporated. The residue was examined by means of gas chromatography (Table V) then distilled to give 3.68 g. of recovered olefin, b.p. 121–122°; 0.56 g. of an intermediate fraction, b.p. 122–191°; 6.45 g. of 2-octyl formate, b.p. 181–183° (lit.²⁶ b.p. 81–82° (20 mm.)); and 0.2 g. of pot residue. The infrared spectrum of the olefin fraction was identical in every major respect with that of authentic 1-octene. The ester fraction was treated with excess lithium aluminum hydride in ether, and the recovered alcohol was distilled. This product gave a single elution peak in gas chromatography and its infrared spectrum was like that of authentic 2-octanol except for an unidentified peak at 7.53μ which was not present in the spectrum of authentic 3- or 4-octanol, nor in that of the formate before treatment with lithium aluminum hydride, and thus seems to be due to accidental contamination of the sample or sample cell.

(26) R. H. Pickard, J. Kenyon and H. Hunter, *J. Chem. Soc.*, **123**, 1 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Some Condensations at the Methylene and Terminal Methyl Groups of Benzenesulfonylacetone Through its Mono- and Dipotassio Salts^{1,2}

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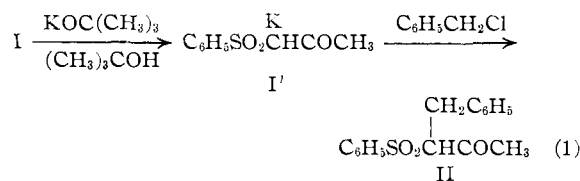
Benzenesulfonylacetone was benzylated and benzoylated at its methylene group through its monopotassio salt to form the C-benzyl and O-benzoyl derivatives, respectively. The benzyl derivative was coupled with benzenediazonium chloride to give an azo compound, whereas benzenesulfonylacetone was converted by this reagent to a phenylhydrazone. Benzenesulfonylacetone was benzylated and benzoylated at its terminal methyl group through its dipotassio salt to form the corresponding C-derivatives. The dipotassio salt was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. The benzoyl derivative was cyclized with hydrazine to give a pyrazole, nitrosated with nitrous acid to produce an oxime, and independently synthesized from 1-bromobenzoylacetone and sodium benzenesulfinate.

Benzylation and benzoylation at the methylene and terminal methyl groups of benzoylacetone have been effected previously through its mono- and dialkali salts, respectively.⁴

In the present investigation such condensations at the methylene and terminal methyl groups of benzenesulfonylacetone (I) were effected.

Results with Monopotassio Salt of I.—Because I is similar to β-diketones having a reactive methylenic⁵ or methinyl hydrogen,⁶ it was converted by potassium *t*-butoxide in *t*-butyl alcohol to its monopotassio salt I', which was alkylated with benzyl chloride in this medium to give the methylene derivative II in 75% yield (eq. 1).

That the product was the expected C-benzyl derivative II and not the possible O-benzyl derivative was shown by its infrared spectrum, which



gave a strong band at 5.8 μ for the carbonyl group.⁷ Moreover the product gave a positive carbonyl group test with 2,4-dinitrophenylhydrazine.

Structure II was further established by coupling it with benzenediazonium chloride in the presence of sodium acetate to form azo derivative III. Also the original sulfone-ketone I reacted with this reagent but the resulting azo derivative underwent isomerization to give phenylhydrazone IV.⁸ Methylene substituted and unsubstituted β-diketones are known to undergo analogous reactions to produce the corresponding azo compound and phenylhydrazone, respectively.⁹ For example, acet-

(7) See L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 132.

(8) Only one of the two possible geometric isomers appeared to be obtained; its structure was not determined.

(9) See S. M. Farmerter, "Organic Reactions," Vol. X, John Wiley and Sons, Inc., New York, N. Y., 1959, Chap. 1.

(1) Supported by the U. S. Army Research Office (Durham).

(2) Reported at the Cleveland, Ohio, Meeting of the American Chemical Society, April, 1960.

(3) On leave from the University College, Dublin, Ireland.

(4) See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

(5) See D. F. Martin, W. C. Fernelius and M. Shamma, *ibid.*, **81**, 130 (1959).

(6) See P. J. Hamrick, C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).