

tions 50-59 gave 260 mg (1.17 mmol) of unreacted benzophenone hydrazone, mp 95-96° (lit.²⁸ mp 98°).

Direct Irradiation of Benzophenone Hydrazone (2) in Methanol.—Benzophenone hydrazone (476 mg, 2.46 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that no filter was used and the irradiation time was extended to 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 7-10 yielded 28 mg (0.17 mmol, 16%) of diphenylmethane, identified by ir and nmr spectroscopy. Fractions 35-39 gave 33 mg (0.18 mmol, 17%) of benzophenone, identified by ir spectroscopy. Fractions 45-51 gave 83 mg (0.46 mmol, 44%) of benzophenone imine, identified by ir spectroscopy and by spontaneous conversion to benzophenone upon standing. Fractions 52-59 produced 273 mg (1.39 mmol) of unreacted benzophenone hydrazone, mp 94-97°.

Vycor-Filtered Irradiation of Benzophenone Hydrazone (2) in Benzene.—Benzophenone hydrazone (339.1 mg, 1.73 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that benzene was the reaction solvent and the irradiation time was extended to 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 5-10 gave 69 mg of material whose ir spectrum indicated it to be impure diphenylmethane. These fractions were rechromatographed (see following paragraph). Fractions 29-34 afforded 56 mg (0.31 mmol, 45%) of benzophenone, identified by ir spectroscopy. Fractions 43-50 produced 204 mg (1.04 mmol) of unreacted benzophenone hydrazone, mp 92-94°.

Rechromatography of fractions 5-10 under the same conditions

(28) T. Curtius and E. Rauterberg, *J. Prakt. Chem.*, **44** [2], 194 (1891).

gave 39 mg (0.23 mmol, 39%) of diphenylmethane, identified by ir spectroscopy, in fractions 5-8.

Vycor-Filtered Irradiation of Benzophenone Hydrazone (2) in Methanol Containing Sodium Hydroxide.—Benzophenone hydrazone (398 mg, 2.03 mmol) and sodium hydroxide (20 mg, 0.50 mmol) were irradiated in the same manner as described for the Vycor-filtered irradiation of 1 in methanol. The chromatographic analysis of the reaction mixture was also conducted in the same manner.

Fractions 6-8 afforded 53 mg (0.32 mmol, 31%) of diphenylmethane, identified by ir spectroscopy. Fractions 29-31 gave 9 mg (0.05 mmol, 5%) of benzophenone, identified by ir spectroscopy. Fractions 33-39 produced 89 mg (0.49 mmol, 48%) of benzophenone imine, identified by ir spectroscopy and by conversion to benzophenone upon standing. Fractions 42-52 gave 197 mg of unreacted benzophenone hydrazone (2), mp 90-94°.

Pyrex-Filtered Irradiation of Benzophenone and Hydrazine in Benzene.—Benzophenone (180 mg, 1.00 mmol) and hydrazine (128 mg, 4.00 mmol) were irradiated in the same manner as described for the Pyrex-filtered irradiation of 1 except that benzene was the solvent. The ir spectrum of the crude reaction mixture was the same as that of benzopinacol.

Registry No.—1, 588-64-7; 2, 5350-57-2; 3, 966-88-1; 4, 574-61-8; 5, 3746-21-2.

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Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. IV. Rearrangement Studies of Trimethylacetaldehyde-1-¹⁴C and 3-Methyl-2-butanone-2-¹⁴C¹

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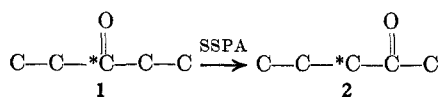
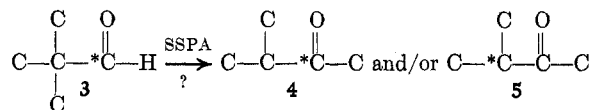
Received December 22, 1969

Solid supported phosphoric acid (SSPA) treatment of trimethylacetaldehyde-1-¹⁴C at 230° gives 3-methyl-2-butanone-2-¹⁴C (4) and no 3-methyl-2-butanone-3-¹⁴C (5); no oxygen-function rearrangement takes place. Further SSPA treatment of 4 did not result in rearrangement to 5. These and related experiments where oxygen-function rearrangement does take place are rationalized in terms of relative stabilities of proposed carbonium ion intermediates.

Solid supported phosphoric acid (SSPA) is an effective catalyst for the rearrangement of aldehydes and ketones to isomeric ketones.² In agreement with previous work,³ trimethylacetaldehyde was found² to rearrange quantitatively to 3-methyl-2-butanone.

Since the 2-pentanone formed from 3-pentanone-3-¹⁴C (1) by SSPA treatment had all of the carbon-14

the SSPA-catalyzed rearrangement of trimethylacetaldehyde to 3-methyl-2-butanone.



label in the 3 position,⁴ it was of interest to see if a similar oxygen-function rearrangement would take place in

Trimethylacetaldehyde-1-¹⁴C (3), synthesized by the method of Brown and Tsukamoto,⁵ was passed once through a SSPA column² at 230°, and the resulting 3-methyl-2-butanone-X-¹⁴C was degraded to isopropyl acetate by *m*-chloroperbenzoic acid oxidation. Derivatives of the acid and alcohol parts of the ester were prepared and assayed for radio activity. The results of these experiments are shown in Table I.

Since all of the radioactivity was found in the acetanilide and none in the isopropyl derivative, it is clear that oxygen-function rearrangement does not take place during the conversion of trimethylacetaldehyde to 3-methyl-2-butanone, *i.e.*, 3 → 4 and not 5.

(1) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234. Paper III in this series: F. Juge and A. Fry, *J. Org. Chem.*, **35**, 1876 (1970).

(2) W. H. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

(3) S. N. Danilov and E. D. Venus-Danilova, *Ber.*, **59B**, 377 (1926); H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniar, *ibid.*, **69B**, 2244 (1936).

(4) A. Fry and W. H. Corkern, *J. Amer. Chem. Soc.*, **89**, 5894 (1967).

(5) H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 4549 (1961).

TABLE I
ACTIVITY RESULTS (MILlicURIE/MOLE) FOR THE SSPA REARRANGEMENT OF TRIMETHYLACETALDEHYDE-1-¹⁴C
TO 3-METHYL-2-BUTANONE-X-¹⁴C

Expt	Trimethylacetaldehyde-1- ¹⁴ C ^a	3-Methyl-2-butanone-X- ¹⁴ C ^a	Acetanilide	Isopropyl 3,5-dinitrobenzoate
1	0.0087 ± 0.00005	Not determined	0.0086 ± 0.00003	0.0001 ^b
2	0.364 ± 0.001	0.365 ± 0.005	0.365 ± 0.001	0.0008 ± 0.00007

^a The activities of the aldehyde and ketone were determined on the semicarbazone derivatives. ^b Indistinguishable from the counting rate for blank samples.

TABLE II
ACTIVITY RESULTS (MILlicURIE/MOLE) OBTAINED BY REPEATED PASSAGE OVER SSPA CATALYST AT 230° OF THE
3-METHYL-2-BUTANONE FORMED FROM TRIMETHYLACETALDEHYDE-1-¹⁴C

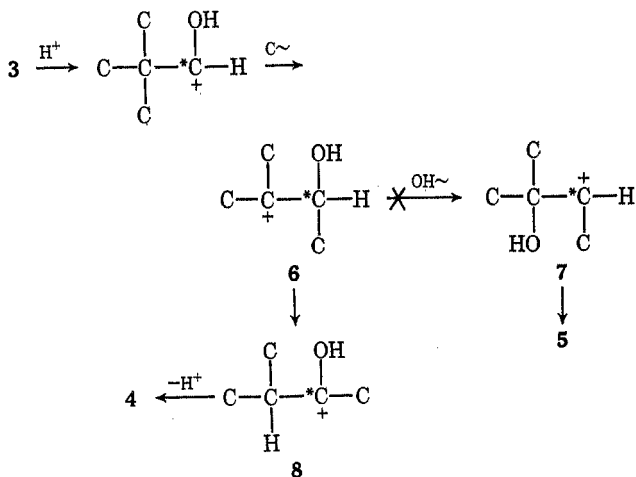
No. of passes over SSPA	Recovered material, ml	Removed for degradation, ml	Acetanilide	Isopropyl 3,5-dinitrobenzoate
0 ^a	32			
1	28	6	0.206 ± 0.001	0.0004 ± 0.0001
2	20			
3	20	5	0.205 ± 0.001	0.0005 ± 0.0001
4	13			
5	13			
6	13	5	0.206 ± 0.001	0.001 ± 0.0001
7	7			
8	7			
9	5	5	0.206 ± 0.001	0.001 ± 0.0001

^a The radioactivity of trimethylacetaldehyde-1-¹⁴C used was 0.206 ± 0.001 mCi/mol, and 3-methyl-2-butanone obtained after one pass was 0.206 ± 0.001 mCi/mol. The activities of the aldehyde and ketone were determined on the semicarbazone derivatives.

The possibility that the first formed 3-methyl-2-butanone-2-¹⁴C (4) might undergo oxygen-function rearrangement (equilibration of 4 and 5) upon longer exposure to the SSPA catalyst was then checked with the results shown in Table II.

Again, all of the radioactivity remains in the carbonyl group; 4 does not equilibrate with 5; oxygen-function rearrangement is not observed, in sharp contrast to the formation of 2 from 1. The possibility that 4 would form 5 at the higher temperature (340° compared with 230°) used⁴ in the conversion of 1 to 2 could not be checked because such branched-chain compounds decompose readily at the higher temperature.²

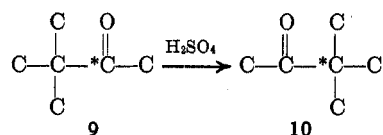
The most likely path for the rearrangement of 3 to 4 may be depicted as follows,⁶ the critical question being the relative rate of hydrogen migration (6 → 8) *vs.* oxygen-function rearrangement (here depicted as OH migration for simplicity) (6 → 7). It may be noted that 6 → 7 involves the energetically unfavorable con-



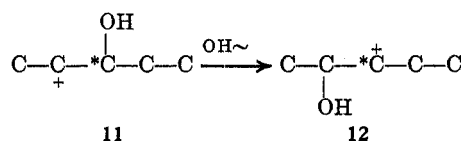
(6) In this and the following formulations, the ions are shown as open carbonium ions without specific discussion at this time of the accompanying solvation, counterions, etc.

version of a tertiary carbonium ion (3° R⁺) to a secondary carbonium ion (2° R⁺) while 6 → 8 represents the energetically more favorable conversion of a 3° R⁺ to a highly stabilized ketone conjugate acid.

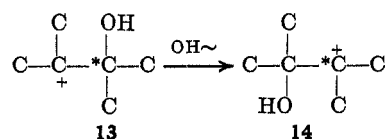
The lack of oxygen-function rearrangement in 4, its presence⁴ in 1 → 2, and its presence⁷ in the sulfuric acid catalyzed rearrangement of 3,3-dimethyl-2-butanone-2-¹⁴C (9) to 3,3-dimethyl-2-butanone-3-¹⁴C (10) may be



rationalized in a similar fashion. In 1 → 2, the process corresponding to the energetically unfavorable 3° R⁺ 6 → 2° R⁺ 7 involves interconversion of two energetically similar 2° R⁺, 11 → 12, while in 9 → 10, the cor-



responding step involves interconversion of two energetically identical 3° R⁺, 13 → 14.



Experimental Section

Trimethylacetaldehyde-1-¹⁴C (3).—Trimethylacetic acid-1-¹⁴C was prepared by carbonation of *t*-butylmagnesium chloride with carbon-14 dioxide by standard methods. The acid was converted to the acid chloride by exchange with benzoyl chloride,⁸ and then to trimethylacetaldehyde-1-¹⁴C, bp 72–74° (730 mm) [lit.⁵ bp

(7) K. Bhatia and A. Fry, *J. Org. Chem.*, **34**, 806 (1969).

(8) H. C. Brown, *J. Amer. Chem. Soc.*, **60**, 1325 (1938).

73–75° (740 mm)], semicarbazone mp 190° (lit.⁹ mp 191°) by the method of Brown and Tsukamoto.⁵ The radiochemical purity of **3** is adequately demonstrated by the agreement in the radioactivity values for **3** and **4** and by the excellent activity balances in the degradation products of **3** and **4** as shown in Tables I and II.

Rearrangement of Trimethylacetaldehyde-1-¹⁴C and Treatment of 3-Methyl-2-butanone-2-¹⁴C (4) with SSPA.—Preparation of the SSPA catalyst and the general experimental procedure have been described previously.² A column temperature of 230° was used, and, after one pass of 10 ml of **3** over the catalyst, the 8.7 ml of liquid recovered was shown by glpc and nmr analysis to be free of **3** and to consist entirely of 3-methyl-2-butanone, semicarbazone mp 113° (lit.¹⁰ mp 114°). A 32-ml sample of **3** and the products from its rearrangement were passed repeatedly over the SSPA catalyst at 230°. Samples of the material recovered from passes one, three, six, and nine (Table II) were subjected to glpc and nmr analysis, and were degraded to check for oxygen-function rearrangement of the 3-methyl-2-butanone produced in the first pass. Small amounts of impurities were detected in the later fractions, but these were removed in the work-up and degradation procedures.

Degradation of 3-Methyl-2-butanone-2-¹⁴C (4).—Oxidation of **4** to isopropyl acetate and derivative preparation from the ester

(9) S. I. Heilbron, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, p 1214.

(10) Reference 9, p 2144.

were carried out as described previously^{4,7} except that the more stable, commercially available *m*-chloroperbenzoic acid was used instead of perbenzoic acid. The isopropyl acetate was purified by distillation, bp 88° (740 mm) (lit.¹¹ bp 91°), and identified by glpc and nmr comparison with an authentic sample. A careful search (glpc analysis) was made for the isomeric ester, methyl isobutyrate, but none was found. Acetanilide, mp 113.5° (lit.¹² mp 114°), and isopropyl 3,5-dinitrobenzoate, mp 122° (lit.¹³ mp 122°), were obtained from the degradation.

Radioactivity Measurements.—The semicarbazones of **3** and **4** and the acetanilide and isopropyl 3,5-dinitrobenzoate derivatives of the degradation products of **4** were assayed for carbon-14 content using a Beckman LS100 liquid scintillation counter, and the external standard ratio method.¹⁴ The results of the activity determinations are given in Tables I and II. The indicated errors are average deviations of three or more measurements of the same sample.

Registry No.—**3**, 24454-13-5; **4**, 24454-14-6.

(11) R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 302.

(12) Reference 11, p 276.

(13) Reference 11, p 280.

(14) For full details of this procedure, see B. W. Palmer, Ph.D. Dissertation, University of Arkansas, Fayetteville, Ark., 1970.

Reaction of 2-(Δ^3 -Cyclopentenyl)ethyl Bromide with Tri-*n*-butyltin Hydride. Cyclization to Norbornane¹

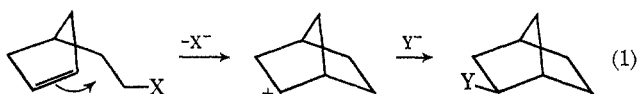
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Received January 28, 1970

The reduction of 2-(Δ^3 -cyclopentenyl)ethyl bromide (**1**) with tri-*n*-butyltin hydride proceeds with some cyclization to norbornane (**3**). At 130° with dilute hydride the cyclization is appreciable. The cyclization process is discussed in terms of purportedly delocalized intermediates in the analogous cationic process. The conclusion is reached that successful cyclization of 2-(Δ^3 -cyclopentenyl)ethyl substrates does not necessarily indicate delocalized intermediates. Rather, a favorable geometry in the transition state for both cationic and radical (but not the anionic) processes rationalizes the data.

The so-called " π route" (1) to the 2-norbornyl and related cations is well documented.² The ring closure



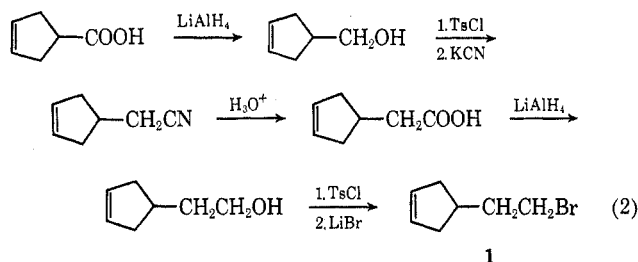
observed in spite of the considerable steric strain involved (estimated³ at 9–19 kcal mol⁻¹) has been taken^{2b} as evidence for the special stability associated with the 2-norbornyl cation, a stability commonly attributed to its supposed nonclassical nature.

Although ring closure of carbon radicals is likewise well documented,⁴ we have found no such study extant

comparable to eq 1. In line with our interest in possible nonclassical radicals,⁵ we studied the 2-(Δ^3 -cyclopentenyl) ethyl radical (1·) to seek ring-closed products.

Results and Discussion

2-(Δ^3 -Cyclopentenyl)ethyl bromide (**1**) was prepared from the corresponding tosylate by treatment with lithium bromide in dry acetone (eq 2). The synthetic



1

sequence proceeded from 3-cyclopentene-1-carboxylic acid and utilized known procedures (see Experimental Section). Bromide **1** so prepared was characterized by

(5) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962); J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967).

(1) Taken from the M.S. Thesis of S. N. M., Loyola University of Chicago, 1969.

(2) (a) R. G. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (d) H. L. Goering and W. D. Closson, *ibid.*, **83**, 3511 (1961); (e) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

(3) Bartlett and Bank^{2b} give the strain energy of the norbornyl ring as "about 19" kcal mol⁻¹ and quote a privately communicated estimate from H. J. Dauben, Jr., as 9.49 kcal mol⁻¹. From heat of combustion data, 18.5 kcal mol⁻¹ appears most reliable: A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(4) For recent references, cf. (a) D. L. Struble, A. L. J. Beckwith, and G. E. Green, *Tetrahedron Lett.*, 3701 (1968); (b) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, **4**, 1603 (1968).