Bridged Polycyclic Compounds. XLVI.[1] Stereochemistry of a Nucleophilic Cyclopropane Ring Opening

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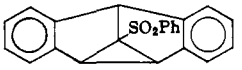
Abstract: 1-Phenylsulfonyldibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (I) and its 2-phenylsulfonyl isomer II were subjected to nucleophilic attack by methoxide and thiophenoxide ion. Only II reacted with these reagents under the conditions utilized. Study of the structures of the products showed that the nucleophilic ring opening of the cyclopropane ring occurred with stereochemical inversion.

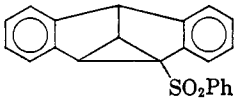
Although nucleophilic ring-opening addition reactions to activated cyclopropanes have been known for some time,[2-8] there appears to be only one case[8] in which the stereochemical course of the ring opening is known. In connection with studies which we have made[9,10] concerned with the stereochemistry of carbanion–intermediate cyclopropane ring closures, it was of interest to us to scrutunize the reverse of this process, nucleophilic ring opening.

Of those cyclopropanes in which ring opening had occurred, none had been activated by conjugation with a sulfonyl group, and the attempts described in the literature to add nucleophiles to cyclopropyl sulfones all failed.[5,11]

As the tricyclooctanes I and II were available to us[9,10] it was of interest to see first if I and II would undergo nucleophilic addition and, if they did, what the stereochemistry of the addition process would be.



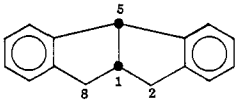
I



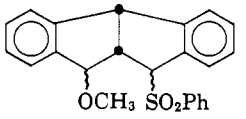
II

Our attempts to add methanol and thiophenol under basic conditions to I failed, whereas both methanol and thiophenol reacted with II under basic conditions at elevated temperatures, but under conditions less severe than those attempted with I. It appears reasonable that the reactivity of II in comparison to that of I is due to the added stabilization of the incipient carbanion by the aromatic ring adjacent to the phenylsulfonyl group.

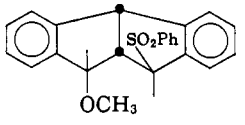
II reacted with methanol only in the presence of base (sodium methoxide was used) and gave only one addition product. The pmr spectrum (in τ values) of the product had three doublets [one proton each at 5.22 (J = 2.3 cps), at 5.36 (J = 4.4 cps), and at 5.70 (J = 7.6 cps)], a multiplet (one proton) at 6.40, and a singlet (three protons) at 6.52, considering absorbances of aliphatic protons only. This pattern is characteristic[13] of the *cis*-dibenzobicyclo[3.3.0]-3,6-octadiene system (III) and is not consistent[14] with the alternative bond cleavage which would lead to a dibenzobicyclo[3.2.1]-octadiene derivative. Thus, the ether sulfone which resulted appeared to be one of the stereoisomers IV. The singlet at τ 6.52 was assigned to the methyl protons of the methoxy group and the broad multiplet centered at τ 6.40 was assigned to the C-1 proton. The doublet (J = 7.6 cps) at τ 5.70 was assigned to the C-5 (benzhydryl) proton because of the previous observation[13] that the hydrocarbon III absorbed at τ 5.44 with J = 7.0 cps.



III



IV



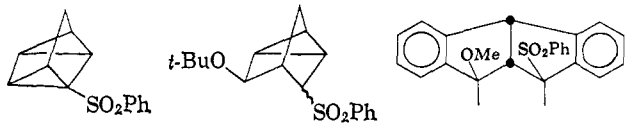
V

The two protons located at C-2 and C-8 then remained to be assigned. At the time the product was first characterized it seemed reasonable that the C-2 and C-8 protons were of the opposite configuration since there was a significant difference (2.3 and 4.4 cps) in their coupling constants with the C-1 proton. It was therefore tentatively (and incorrectly; see below) concluded that the methoxy and phenylsulfonyl groups were *trans* to one another. Since protons α to the phenylsulfonyl group are known[9,10] to be acidic under moderately basic conditions, the C-2 proton could be expected to undergo deuterium exchange with deuterated solvent in the presence of base. In accord with this expectation, treatment with sodium deuterioxide in deuterium oxide–dioxane gave material (containing one deuterium atom) whose pmr spectrum showed the disappearance of the proton with the smaller splitting

(1) Previous paper in series: S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, **89**, 1476 (1967).
(2) W. A. Bone and W. H. Perkin, Jr., *J. Chem. Soc.*, **67**, 108 (1895).
(3) E. P. Kohler and J. B. Conant, *J. Am. Chem. Soc.*, **39**, 1404 (1917).
(4) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952).
(5) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).
(6) T. H. Regan, *ibid.*, **27**, 2236 (1962).
(7) J. M. Stewart and H. H. Westberg, *ibid.*, **30**, 1951 (1965).
(8) J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).
(9) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966).
(10) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967).
(11) It has been reported[12] that hydrogen iodide adds to 1,1-bis(ethylsulfonyl)cyclopropane to give 1,1-bis(ethylsulfonyl)-3-iodopropane. This appears to be a nucleophilic ring opening[5] rather than an electrophilic one in view of the Truce–Lindy results,[5] but represents activation by two sulfonyl groups.
(12) E. Rothstein, *J. Chem. Soc.*, 1560 (1940).
(13) B. B. Jarvis, Ph.D. Thesis, University of Colorado, 1966.
(14) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

constant (J = 2.3 cps) at τ 5.22. A Dreiding model of this system indicated that the protons on the C-2 and C-8 positions that are *cis* to the C-1 proton should have larger splitting constants[15] than those C-2 and C-8 protons that are *trans* to the C-1 proton. On this basis the structure V was assigned to the product.

We were quite unhappy with this assignment, as it indicated that the nucleophilic displacement associated with the cyclopropane ring opening proceeded with retention, rather than with inversion.[16] Theoretical considerations, on the other hand, predict that the cyclopropane ring would be opened with inversion during a nucleophilic attack since the reverse of this process, base-catalyzed ring closure, has shown[9,10,17] a tremendous preference for ring closures with inversion. In other words, the principle of microscopic reversibility would predict that the lowest energy pathway leading to base-catalyzed ring closures would be the lowest energy, and hence most probable, pathway for base-catalyzed ring openings. The assignment was also in conflict with an observation made in our laboratory[18] that the quadricyclyl phenyl sulfone VI[17] was converted by sodium *t*-butoxide to the epimeric (at the sulfone carbon atom) *exo*-*t*-butoxynortricyclyl sulfones VII, which result from ring opening with inversion. When the Meinwald–Crandall work was published,[8] this also was inconsistent with the assignment.



VI VII VIII

Models of the *cis*[3.3.0] system show that the *anti*-2 and -8 bonds point away from each other while the *syn*-2 and -8 bonds point in toward each other. On this basis, it appeared likely that the most stable epimer of IV would be the *anti,anti*-2,8-disubstituted derivative VIII or that at least a mixture of VIII and *anti,syn*-2,8-disubstituted compounds would result from epimerization. Therefore, several attempts were made to epimerize the methoxy group in the presumed V using concentrated sulfuric acid in methanol (no reaction) and boron trifluoride etherate in methylene chloride (resulted in decomposition). Since the methyl ether resisted attempts to cause epimerization, an effort was made to synthesize the corresponding alcohol by adding water to II in the presence of base. Unfortunately, several attempts to add water across the 2,8 bond of II failed.

Although there were no exchange experiments conducted to show that we had in fact produced a cationic intermediate in the attempted epimerization of the methoxy ether group, we felt that it was likely that such a benzylic cation should have formed under the conditions used, and this served to increase our concern about the assignment of the stereochemistry at C-8.

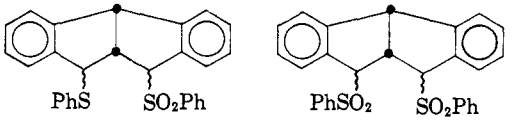
(15) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); however, see M. Karplus, *J. Am. Chem. Soc.*, 85, 2870 (1963). For a recent survey on conformational effects on coupling constants see: R. J. Abraham in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., London, 1967, pp 138–144.

(16) The configuration at the phenylsulfonyl carbon (C-2) atom is not of theoretical interest, as it is the result of thermodynamic, rather than kinetic, control.

(17) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, 88, 1529 (1966).

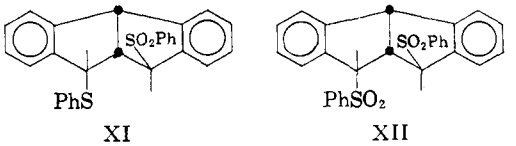
(18) M. S. Singer, Ph.D. Thesis, University of Colorado, 1966.

It therefore seemed worthwhile to study the ring opening of II utilizing thiophenoxide ion as nucleophile. This should result in the formation of one or more of the epimers of IX, and oxidation of the product(s) would lead to the analogous disulfone(s) X. Here it seemed reasonable to assume that pmr spectra would enable us to distinguish between the three possible diastereoisomeric disulfones.



IX X

In the presence of ethanolic base, thiophenol added to II to give a thiophenoxy sulfone whose pmr spectrum resembled that of the methyl ether rather closely. There was a broad multiplet (one proton) at τ 6.47, assignable to the C-1 proton, a doublet (one proton, J = 2.3 cps) (which disappeared on exchange with deuterated solvent in the presence of base) at τ 5.47, assignable to the C-2 proton, and two doublets (one proton each) centering at τ 5.80 which crossed over one another. The assignments for these two closely spaced protons were based on the following facts. It was obvious from inspection that one of the protons (at C-5 or at C-8) gave rise to the center two lines (J = 4.0 cps) and the other to the outer lines (J = 10.0 cps), or that one gave rise to the first and the third line (J = 6.4 cps), the other to the second and fourth line (J = 7.2 cps). Exchange of the C-2 proton (α to the phenylsulfonyl group) for a deuterium atom produced a simplified spectrum in which the C-1 proton now gave rise to what appeared to be a triplet. This is reasonable only if the C-5 and C-8 protons split with the C-1 proton with J values of the same order, *i.e.*, J = 7.2 cps and J = 6.4 cps. The larger coupling constant was assigned to the C-5 proton since this proton has consistently exhibited a coupling constant between 7 and 8 cps.[13] Again it is significant that the C-2 proton (J = 2.3 cps) and the C-8 proton (J = 6.4 cps) exhibited quite different coupling constants with the C-1 proton, thus implying that the thiophenoxy and phenylsulfonyl groups were *trans* to one another. Since the proton with the smaller J value disappeared upon exchange with a deuterium atom, the same argument that was applied to the methanol addition product could be applied to the thiophenol addition product and, therefore, the structure XI was assigned to it.

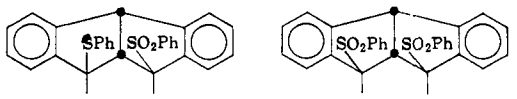


XI XII

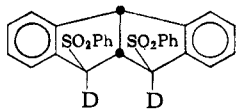
Oxidation of XI would give the bis(phenyl sulfone) XII. However, oxidation of the actual product with *m*-chloroperbenzoic acid in acetic acid gave a bis(phenylsulfonyl) compound whose pmr spectrum was inconsistent for that anticipated for XII. It had a doublet of triplets (one proton) at τ 6.23 (J = 4.6, 7.2 cps), assignable to the C-1 proton, a doublet at τ 5.64 (one proton, J = 7.2 cps) assignable to the C-5 proton, and one doublet at τ 5.23 (two protons, J = 4.6 cps), assignable to the C-2 and C-8 protons. The spectrum is consistent

only with a compound having both phenylsulfonyl groups *cis* to each other (*e.g.*, XIV).

The oxidation was repeated using hydrogen peroxide in acetic acid followed by the usual work-up in water except that the basic wash (10% sodium carbonate solution) was omitted; the results were identical with those of the first oxidation. To make certain that the sulfone was not undergoing epimerization under the reaction conditions, the bis(phenylsulfonyl) compound was treated with O-deuterated acetic acid under the reaction conditions and was quenched in deuterium oxide. This led to no incorporation of deuterium into the molecule. Oxidation was also carried out in methanol to give XIV. Thus, one must conclude that in the addition product the thiophenoxy and phenylsulfonyl groups were *cis* to each other and, in fact, the structure was really XIII, and that of the oxidation product was XIV. The fact that equilibrium position of the phenylsulfonyl groups in X is almost entirely *anti* was evident from the lack of epimerization of XIV when treated with sodium ethoxide in ethanol, conditions which were certainly sufficient to cause any possible epimerization of the phenylsulfonyl groups.[9,10,16] Such treatment of XIV with sodium deuterioxide in deuterium oxide–dioxane gave the anticipated product of deuterium exchange, XV. The phenylsulfonyl groups in XIV were assigned *anti* based on the models of this system, which suggest that a pair of *syn* sulfonyl groups would be under tremendous steric compression, and would therefore be transformed rapidly by base to *anti* positions.



XIII XIV



XV

These results make it clear that the assignment of structure V to the methanol addition product is without merit and make it likely that structure VIII is instead the correct one. It is evident that one must be cautious in assigning configurations of groups at C-2 and C-8 positions in this system based upon coupling constants in the pmr spectra as these values appear to be markedly dependent upon the type (and probably the size) of the groups present.[19]

Our stereochemical results would thus appear to be consistent with the concept that ring-opening attack by nucleophile upon cyclopropane rings occurs with inversion of configuration.

Experimental Section

Spectra. The pmr spectra were determined with saturated solutions in either carbon tetrachloride or deuteriochloroform on a Varian A-60 instrument, and results are expressed in τ units, where τ = 10.00 for the internal standard tetramethylsilane. J values reported are "observed" ones.

(19) The *cis*-bicyclo[3.3.0]-3,6-octadiene system is not a particularly rigid one, as judged from Dreiding models, and the large phenylsulfonyl groups may distort the ring system substantially. Judging from coupling constants, this group distorts even the very rigid norbornane ring system.[20]

(20) S. J. Cristol and T. W. Russell, unpublished work.

Preparation of *anti*-2-Phenylsulfonyl-*anti*-8-methoxy-*cis*-dibenzobicyclo[3.3.0]-3,6-octadiene (VIII). Sealed in a thick-walled glass tube was 1.0 g (2.9 mmoles) of 2-phenylsulfonyldibenzotricyclo-[3.3.0.$0^{2,8}$]-3,6-octadiene (II)[10] and 20 ml of absolute methanol in which 200 mg of sodium metal had been dissolved. This mixture was heated at 140° for 20 hr. The tube was opened, and the contents were poured into 100 ml of water. The mixture was extracted with 100 ml of ether. The ethereal solution was washed with water, decolorized with activated charcoal, and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting oil was crystallized from 95% ethanol to give 1.0 g (93%) of VIII, mp 134–135°.

The pmr spectrum of VIII in deuteriochloroform showed doublets (one proton each) at τ 5.22 (J_{12} = 2.3 cps), at 5.36 (J_{18} = 4.4 cps), and at 5.70 (J_{15} = 7.6 cps), a sharp singlet (three protons) at τ 6.52, a broad multiplet (one proton) centered at τ 6.40, and a multiplet for aromatic protons from τ 2.1 to 3.0 (13 protons).

Anal. Calcd for $C_{23}H_{20}O_3S$: C, 73.38; H, 5.36. Found: C, 73.26; H, 5.50.

Attempted Epimerizations of the Methyl Ether VIII. When VIII was treated in methylene chloride with 1 or more equiv of boron trifluoride etherate, the pmr spectrum of the reaction mixture after water work-up and ether extraction showed no identifiable material. Less than 1 equiv of boron trifluoride led to less decomposition but still no observable (pmr spectrum) amount of epimerization. Treatment of 150 mg of VIII with 0.5 ml of concentrated sulfuric acid in 15 ml of absolute methanol at reflux for extended periods of time gave no reaction and VIII was recovered unchanged.

Deuterium Exchange of the C-2 Proton in VIII. In 1 ml of deuterium oxide and 1 ml of dry dioxane was dissolved 25 mg of sodium metal. To this solution was added 3 ml of dry dioxane in which 70 mg of the methyl ether VIII had been dissolved. The resulting mixture (two phases) was shaken at about 70° for 5 min and then poured into 50 ml of water. The mixture was extracted with 50 ml of ether. The ethereal solution was washed several times with water and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation and a pmr spectrum of the resulting oil showed the disappearance of the proton located at τ 5.22. The material was crystallized from 95% ethanol to give 55 mg of *syn*-2-deuterio-*anti*-2-phenylsulfonyl-*anti*-8-methoxy-*cis*-dibenzobicyclo-[3.3.0]-3,6-octadiene, mp and mmp with VIII 134–135°.

Preparation of *anti*-2-Phenylsulfonyl-*anti*-8-thiophenoxy-*cis*-dibenzobicyclo[3.3.0]-3,6-octadiene (XIII). Sealed in a thick-walled glass tube was 700 mg (2.03 mmoles) of the sulfone II, 1 ml of thiophenol, and 17 ml of absolute ethanol in which 200 mg of sodium metal had been dissolved. This mixture was heated at 140° for 4 hr. The tube was opened and the contents poured into 100 ml of water. This mixture was extracted with 100 ml of ether. The ether was dried with anhydrous magnesium sulfate, and the ether was then removed by rotary evaporation. The resulting oil was passed over 60 g of Merck 71695 acid-washed alumina. Thiophenol was eluted with petroleum ether (bp 30–60°) and 900 mg (97%) of thiophenoxy sulfone XIII came off the column with 40% anhydrous ether in petroleum ether. It was recrystallized from petroleum ether–ether to give 750 mg (83%) of XIII, mp 126–128°. Recrystallization from petroleum ether–ether of the 126–128° compound gave XIII, mp 171–173°. Several recrystallizations of this gave XIII, mp 172–173°. Apparently XIII exists in two forms, as the infrared and pmr spectra of the two forms in solution were identical.

The pmr spectrum of XIII in carbon tetrachloride showed doublets (one proton each) at τ 5.47 (J_{12} = 2.3 cps), at 5.77 (J_{18} = 6.4 cps), and at 5.81 (J_{58} = 7.2 cps), a broad multiplet (one proton) at τ 6.47, and a multiplet due to aromatic protons from τ 2.0 to 3.0 (18 protons).

Anal. Calcd for $C_{28}H_{22}O_2S_2$: C, 73.97; H, 4.88. Found: C, 73.80; H, 4.96.

Deuterium exchange of the C-2 proton in XIII was carried out in the same manner as the C-2 proton was exchanged for deuterium in the methyl ether VIII. The pmr spectrum of the resulting compound showed the disappearance of the proton located at τ 5.47 and the broad multiplet at τ 6.47 became resolved into an unsymmetrical triplet. *syn*-2-Deuterio-*anti*-2-phenylsulfonyl-*anti*-8-thiophenoxy-*cis*-dibenzobicyclo[3.3.0]-3,6-octadiene was recrystallized from petroleum ether–ether, mp 172–173°, undepressed with XIII.

Preparation of *anti*-2-*anti*-8-Bis(phenylsulfonyl)-*cis*-dibenzobicyclo-[3.3.0]-3,6-octadiene (XIV). To a solution of 10 ml of glacial acetic acid containing 300 mg (0.66 mmole) of thioether XIII was added 500 mg (85% minimum assay, FMC Corp., Carteret, N. J., 2.5

mmoles) of *m*-chloroperbenzoic acid. This mixture was heated at 70° for 10 min and then poured into 50 ml of water. The water was extracted with 50 ml of ether. The ether was washed with water and with 10% sodium carbonate solution and was then dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol to give 280 mg (90%) of XIV, mp 224–225°.

The pmr spectrum of XIV in deuteriochloroform showed doublets at τ 5.23 (two protons, J_{12} = 4.6 cps) and at 5.64 (one proton, J_{15} = 7.2 cps), a doublet of triplets centered at τ 6.23 (one proton), and a multiplet due to aromatic protons from τ 1.9 to 3.0 (18 protons).

Anal. Calcd for $C_{28}H_{22}O_4S_2$: C, 69.12; H, 4.56. Found: C, 69.29; H, 4.60.

Oxidation of the thioether XIII with excess hydrogen peroxide in acetic acid followed by the usual work-up but omitting the 10% sodium carbonate wash gave results identical with those obtained with the *m*-chloroperbenzoic acid oxidation.

When 90 mg of the sulfone XIV was heated in 3 ml of glacial acetic acid-O-*d* (90% monodeuterated) at 70° for 10 min, then poured into 5 ml of deuterium oxide (99.5% minimum assay), and then extracted with 10 ml of anhydrous ether, a pmr spectrum of the resulting solid showed no deuterium incorporation into XIV.

Deuterium exchange of the benzylic protons was carried out in the same manner as the exchange reactions with the methyl ether VIII and the thioether XIII. *syn*-2,*syn*-8-Dideuterio-*anti*-2,*anti*-8-bis(phenylsulfonyl)-*cis*-dibenzobicyclo[3.3.0]-3,6-octadiene (XV) was obtained in 88% yield and was recrystallized from 95% ethanol, mp 224–225°, undepressed with XIV. The pmr spectrum in deuteriochloroform showed doublets (one proton each) at τ 5.64 and at τ 6.23 (J_{15} = 7.2 cps) and a multiplet due to 18 aromatic protons from τ 1.9 to 3.0.

Treatment of 150 mg of the bis(phenyl sulfone) XIV for 10 min in a refluxing solution of 50 mg of sodium metal dissolved in 1 ml of dioxane and 7 ml of absolute ethanol gave no reaction. Only starting material (130 mg) was recovered, mp and mmp 224–225°.

Oxidation of the Thioether XIII with Hydrogen Peroxide in Methanol. To a solution of 50 mg (0.1 mmole) of XIII in 10 ml of methanol held at reflux was added 1 ml of 30% hydrogen peroxide. This mixture was heated at reflux for 1 hr whereupon an additional 1 ml of 30% hydrogen peroxide was added. The resulting solution was heated at reflux for an additional 2 hr, cooled, and poured into 50 ml of a 5% sodium bisulfite solution. The mixture was extracted well with ether, and the ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and a pmr spectrum of the resulting oil showed no starting material present and indicated the presence of only XIV. The sample was crystallized from 95% ethanol to give 30 mg (60%) of XIV, mp and mmp 224–225°.

Attempted Addition of Thiophenol and Methanol to 1-Phenylsulfonyldibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (I). When the cyclopropyl sulfone I was treated under the same reaction conditions as the cyclopropyl sulfone II was treated, neither thiophenol nor methanol reacted with I. The use of higher temperatures (up to 180°) and longer periods of time (up to 3 days) still led to no observable (pmr spectra) reaction although the reaction mixtures became very dark.

Attempted Nucleophilic Addition of Water to the Cyclopropyl Sulfone II. When 1 g of II was treated with 190 mg of potassium hydroxide dissolved in 5 ml of water and 5 ml of dioxane in a sealed tube at 180° for 30 hr, no observable (pmr spectra) reaction took place. The use of varying amounts of water and dioxane had no effect upon the reaction. The use of *t*-butyl alcohol in conjunction with water and dioxane still had no effect on the course of the reaction.

Acknowledgments. This work was supported in part by Public Health Service Grant GM-12139, from the Institute of General Medical Sciences. B. B. J. also wishes to acknowledge, with thanks, fellowship support from the Shell Companies Foundation, Inc.

Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. I. The Scope and Mechanisms of Ketone Rearrangements[1a]

Walter H. Corkern[1b] and Arthur Fry

Contribution from the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. *Received December 30, 1966*

Abstract: Open-chain aliphatic ketones and some aldehydes can be rearranged easily with a high recovery of fairly extensively rearranged material by passing the carbonyl compound over a bed of solid supported phosphoric acid catalyst at elevated temperature. The rearrangement products are usually accompanied by numerous low retention time materials. It was found that ketones which have branching adjacent to the carbonyl group rearrange at lower temperatures than their straight-chain isomers. However, the branched-chain ketones decompose readily at temperatures which result in good yields of rearrangement products from the straight-chain ketones. Several carbonium ion type mechanisms are suggested for the reaction, and for cases where more than one product might be obtained, the one expected from the path which involves the most stable carbonium ions is always the major rearrangement product.

Most recent research on acid-catalyzed ketone rearrangements has been carried out in homogeneous solutions in sulfuric or perchloric acid.[2] In order to obtain extensive rearrangement in many of these systems, it is necsssary to work at such high temperatures and acid concentrations that most of the starting material is converted to intractable polymeric material. For instance, treatment of 3-pentanone with 72% perchloric acid at 100° for 12 hr resulted in a 1.9% recovery of a mixture of 2- and 3-pentanone containing 12% of the rearranged isomer, 2-pentanone.[3,4]

(1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of W. H. C. and presented in part at the American Chemical Society 20th Southwest Regional Meeting, Shreveport, La., Dec 4, 1964. (b) Monsanto Fellow, 1963–64.

(2) For leading references to recent work, see (a) I. Ookuni and A. Fry, *Tetrahedron Letters*, 989 (1962); (b) T. E. Zalesskaya and T. B. Remizova, *Zh. Obshch. Khim.*, 35, 31 (1965).

(3) A. Fry, I. Ookuni, G. J. Karabatsos, J. D. Graham, and F. Vane, *J. Org. Chem.*, 27, 1914 (1962).