(lactones) rather than epoxides when there is an opportunity for appreciable interaction between the two functional groups. The formation of allylically isomeric esters (lactones) is also to be anticipated.

Acknowledgment.—This work was supported in part by a research grant from the National Science Foundation. This support is acknowledged with pleasure.

Experimental

Reaction of Dehydronorcamphor (II) with Peracetic Acid.—A solution of 5.4 g. of sodium acetate in 27 ml. of 40% peracetic acid was added slowly to a stirred solution of 10 g. of dehydronorcamphor in 15 ml. of chloroform. During the addition the temperature of the reaction mixture was not allowed to rise above 0°, and this temperature was maintained for one hour after the addition had been completed. The reaction mixture was neutralized with 40% sodium hydroxide solution, again maintaining a 0° temperature. The organic product was extracted into ether, the ether dried over anhydrous magnesium sulfate, and the product was distilled under reduced pressure after removal of the solvents. A single product, b.p. 131–132° (22 mm.), $n^{25}D$ 1.4908, d^{25} 1.1642, was obtained in 56% yield (6.4 g.). This product showed infrared maxima in the carbonyl region at 5.65 and 5.80 μ.

Anal. Calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.77.

In some subsequent experiments, a similar product missing the 5.80 μ band was obtained. Furthermore, slow distillation of the original material showing both carbonyl peaks gave rise to fractions all of which showed diminished intensities at 5.80 μ. Finally, treatment of the mixture with sulfuric acid, or even chromatography on Magnesol–Celite, caused complete conversion to the 5.65 μ form.

Anal. Calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.60; H, 6.61.

Quantitative Hydrogenation of Lactone Mixture (VI + IX).—A methanol solution of 0.151 g. of the lactone mixture obtained above was hydrogenated over prereduced Adams catalyst. After 10 minutes, 97% of the total hydrogen had been taken up. The reaction was stopped after 40 minutes. A total of 60.5 ml. of hydrogen (29° and 738 mm.), corresponding to 1.94 moles per mole of lactone, was absorbed.

Hydrogenation of Lactone IX.—A solution of 5 g. of lactone IX in methanol was hydrogenated over prereduced Adams catalyst in a Parr apparatus for 2 hours. After removal of solvent, 4.4 g. of product was collected, b.p. 101–106° (5 mm.). This material was dissolved in ether and extracted with 10% sodium hydroxide solution.

The ether solution was dried over anhydrous magnesium sulfate. Upon removal of the ether a liquid residue remained which showed a single carbonyl peak at 5.65 μ, yield 0.30 g. (6%). This was shown to be lactone X by comparison with an authentic sample prepared as described by Linstead and Meade[10] using cyclopentadiene as starting material. The infrared spectra and gas chromatograms of the two products were identical; synthesized material, b.p. 121–123° (12 mm.), $n^{25}D$ 1.4727, infrared maxima 2.85, 5.65 μ (lit.[11] b.p. 69° (0.5 mm.), $n^{25}D$ 1.4727, infrared maxima 2.84, 5.69 μ).

The basic aqueous layer was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and the product was distilled under reduced pressure after removal of the solvent. A single fraction b.p. 123–125° (20 mm.), was obtained in 71% yield (3.6 g.). This material was shown to be identical with an authentic sample of cyclopentylacetic acid, prepared according to the method of Verwey,[12] by comparison of infrared spectra. The amides of both acids melted at 150–151°, and no depression of melting point was noted upon admixture of the amides.[13]

Comparison of Infrared Spectra.—When a mixture of unsaturated lactones VI and IX was hydrogenated, the neutral fraction of the hydrogenation product had maxima in the carbonyl region at 5.65 and 5.80 μ. By comparing the spectrum of this mixture (containing X and XI) with that of the pure lactone X it was necessary to attribute several peaks to lactone XI. These peaks occurred at 5.80, 7.27, 8.85, 9.37, 9.83, 11.85 and 12.02 μ. Finally it was shown that an authentic sample of lactone XI showed characteristic absorption bands at these wave lengths.[9]

(10) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(11) W. E. Noland, J. H. Cooley and P. A. McVeigh, THIS JOURNAL, **79**, 2976 (1957).

(12) A. Verwey, *Ber.*, **29**, 1996 (1896).

(13) C. D. Nenitzescu, D. A. Isăcescu and T. A. Volrap, *ibid.*, **71**, 2050 (1938).

ITHACA, N. Y.

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

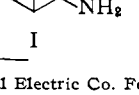
Reactivity of 7-Substituted Camphenes. Structure of β-Isocamphor

BY EUGENE E. VAN TAMELEN AND CLAUDE I. JUDD[1]

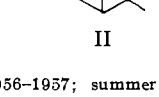
RECEIVED JUNE 9, 1958

β-Isocamphor, the nitrous acid deamination product of camphenamine, has been shown to be *anti*-7-camphenol(Va). The solvolytic behavior of tosylates obtained from *anti*-7-camphenol, *syn*-7-camphenol and *syn*-7-camphanol, has been studied. 2,2,3-Trimethyl-3-cyclohexene-1-carboxaldehyde has been identified as the product resulting from the action of sulfuric acid on β-isocamphor.

More than fifty years ago Duden[2] described the conversion, by successive treatment with phosphorus pentachloride and aqueous alkali, of 3-aminoborenol (I) to the unsaturated base camphenamine, which was shown more recently[3] to be *anti*-7-aminocamphene (II). This finding thus brought the opportunity of studying the 7-camphenyl carbonium ion III, and the present contribution is concerned with several aspects of this reaction system.



I



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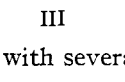


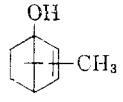
III

(1) General Electric Co. Fellow, 1956–1957; summer assistant, du Pont (1956) and WARF (1957).

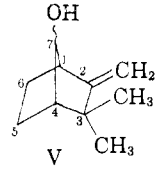
(2) (a) P. Duden and A. E. Macintyre, *Ann.*, **313**, 59 (1900); (b) *Ber.*, **33**, 477 (1900).

(3) E. E. van Tamelen, W. F. Tousignant and P. E. Peckham, THIS JOURNAL, **75**, 1297 (1953).

The first example of 7-carbo-cation formation in this series was provided by Duden,[2] who treated camphenamine sulfate with sodium nitrite and obtained a crystalline product (m.p. 102°) which possessed the molecular formula $C_{10}H_{16}O$ and was named *β-isocamphor*. Initial observations showed the substance to be an unsaturated alcohol; and Duden, prompted by the belief that the hydroxyl group was tertiary and misled by his structural views on camphenamine, assigned to β-isocamphor the structure IV. Because of the conjectural nature of this proposal, the question of structure was reopened; and in view of the propensity of bicyclic terpenoids for skeletal rearrangement, efforts were made to secure rigorous evidence for the constitution of the alcohol.



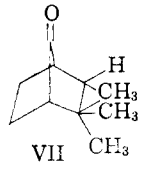
IV



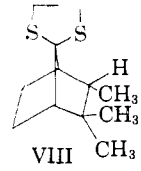
V

Little difficulty was encountered in repeating Duden's directions for the preparation of β-isocamphor, and the properties of the alcohol agreed fairly well with those reported.[2] The infrared spectrum, possessing characteristic bands at 6.03 and 11.3 μ, indicated the presence of a terminal methylene group, and, in fact, the close resemblance to the spectrum of camphenamine suggested that the nitrous acid reaction had involved no structural change other than replacement of the amino group by hydroxyl. This surmise received detailed support in findings which established the nature of the carbon skeleton as well as the position of the alcoholic function of β-isocamphor (V).

Catalytic hydrogenation of β-isocamphor afforded the saturated alcohol, dihydro-β-isocamphor (VI), a crystalline solid melting at 97–98°. Conversion to the corresponding saturated ketone VII was accomplished in high yield by oxidation with chromium trioxide in pyridine. The ketone, characterized as a 2,4-dinitrophenylhydrazone, was

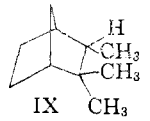


VII

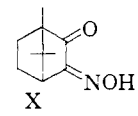


VIII

transformed with ethanedithiol and boron trifluoride etherate to the ethylenethioketal VIII, which, without isolation, was transformed on Raney nickel desulfurization to the known hydrocarbon, isocamphane (IX). Since it is unlikely that the sequence of steps is complicated by skeletal



IX

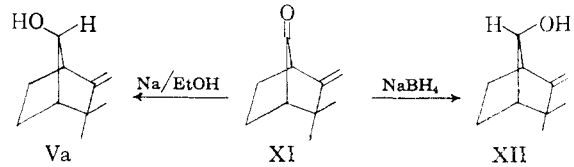


X

rearrangements, the outcome establishes the carbon framework of β-isocamphor.[4]

Because of its conversion to a ketone, the alcohol group in β-isocamphor must be secondary, and thus its position is limited to position 5, 6 or 7 of the camphene skeleton. The 7-position was strongly favored by virtue of the fact that the dihydroketone VII displayed carbonyl band absorption at the abnormally low wave length which distinguishes bicyclo[2,2,1]-7-heptanones from other [2,2,1]bicyclic ketones.[5] By way of confirmation, it was determined that, under conditions where camphor readily is converted to isonitrosocamphor (X), the dihydroketone derived from β-isocamphor provided no such product, thus suggesting that this camphor isomer was not α-methylene ketone. More compelling evidence for the above assignment emerged from hydrogen–deuterium exchange experiments: on treatment with sodium deuteroxide in O-monodeuterioethanol, the saturated ketone did not suffer any exchange of hydrogen. This result unequivocally demonstrates the absence of an enolizable ketone system and is compatible only with the structure assigned (VII), which, because of geometrical constraints imposed by the bridged structure, cannot form a planar, anionic resonance system by proton removal at C-1 or C-4.

In order to complete the structure assignment as well as to provide a secure foundation for studies on the reactivity of β-isocamphor and its derivatives, efforts were made to determine the relative (*syn* or *anti*) configuration of the hydroxyl group. Through reasonable interpretations of various reduction experiments on the ketones derived from β-isocamphor and dihydro-β-isocamphor, it was possible to make a satisfactory assignment. First of all, chromium trioxide oxidation of β-isocamphor in pyridine gave rise to the unsaturated ketone XI, an exceedingly volatile, crystalline substance



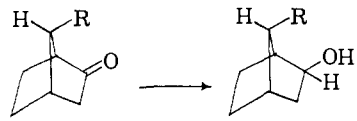
Va XI XII

which readily yielded a dinitrophenylhydrazone and exhibited the carbonyl absorption band at 5.70 μ characteristic of the corresponding saturated case.[6] Reduction of the camphenone with sodium borohydride produced in almost quantitative yield an isomer (XII, m.p. 120.5–122°) of β-isocamphor. That this product was the diastereoisomer was evidenced by its conversion to a *p*-toluenesulfonate, and by its infrared spectrum, which confirmed the presence of the hydroxyl function and revealed that the terminal methylene group was still intact. In view of the well-substantiated rule that steric factors tend to control hydride reduction of hindered keto carbonyl groups (for example, formation of the bicyclic carbinols XV and XVI from ke-

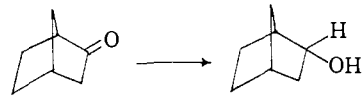
(4) Reduction of the methylene group of β-isocamphor thus takes the same steric course as the reduction of camphene itself, *viz.*, generation of a methyl group with the *endo* configuration (K. Alder and G. Stein, *Ann.*, **525**, 203 (1936)).

(5) C. F. H. Allen, T. Davis, D. W. Stewart and J. A. Van Allan, *J. Org. Chem.*, **70**, 306 (1955).

(6) Duden reported that β-isocamphor was recovered after treatment with chromic acid in acetic acid.



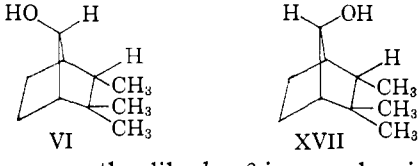
XIII XV



XIV XVI

tones XIII and XIV,[7] respectively),[8] the *syn* relationship (XII) of hydroxyl and substituted ethylene bridge was favored for the new alcohol, and the *anti* configuration (Va) was allotted to β-isocamphor. Because of steric considerations, β-isocamphor may be regarded as the more stable molecule, and it follows that sodium and alcohol, in exercising its usual thermodynamic control of product formation, would, by contrast to sodium borohydride, regenerate this isomer from XI. This prediction was borne out in fact.

Support for these stereochemical assignments took the form of results obtained in carrying out selective reductions of the dihydroketone, 7-isocamphanone (VII), described above. Lithium aluminum hydride or sodium borohydride reduction give rise to an alcohol, m.p. 121.5–122.5°, isomeric with that (VI) obtained by catalytically reducing β-isocamphor. Further, catalytic hydrogenation over platinum in acetic acid containing a small amount of mineral acid, served to convert the isocamphanone to an O-acetate, which on saponification yielded the same alcohol obtained by hydride reduction. In all cases the new alcohol was the only product isolated. On the reasonable assumption that the reducing species approach the ketone from the less hindered side, the resulting alcohol may be assigned the *syn*-configuration XVII,



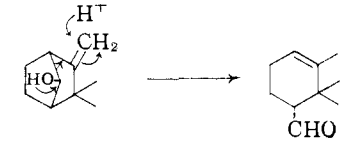
VI XVII

and consequently dihydro-β-isocamphor is formulated as the *anti* isomer VI. Thus, although a rigid assignment based on any single reduction result probably is not warranted, the entire body of evidence is self-consistent and leaves little doubt that the stereochemical structures proposed are correct.

Reactions which generate a carbonium ion at the 7-position of a bicyclo[2,2,1]heptane are of interest for several reasons, including the facts that simple elimination to an olefin as well as stabilization by hydrogen hyperconjugation (XVIII) are

XVIII

formally prohibited by Bredt's rule. The deamination of camphene represents one such case, and a second attempt in this direction involved treatment of β-isocamphor with aqueous alcoholic sulfuric acid. After several days at room temperature there was isolated in good yield a liquid isomer. Readily forming a dinitrophenylhydrazone (XIX), this new substance was formulated as an aldehyde since (1) it displays infrared absorption bands at 3.68 and 5.90 μ, and (2) alkaline silver oxide oxidation afforded an (optically inactive) acid, $C_{10}H_{16}O_2$. With this information available, it became possible to develop a reasonable mecha-



XX XXI

nistic scheme for the acid-catalyzed isomerization: a 1,4-elimination with cleavage (XX) in which the π-electrons of the double bond constitute the "leaving group." In order to secure proof for the structure (XXI) which evolves from this proposal, the derived unsaturated acid XXII was first catalytically reduced; the saturated product was

XXII XXIII

found to be identical with authentic acid of structure XXIII, prepared from *dl*-camphorquinone.[9] The position of the double bond in structure XXI was confirmed by the following findings. The absence of peaks at approximately 6.1 and 11.3 μ in the infrared spectrum of the aldehyde precludes the presence of a terminal methylene group, and the ultraviolet absorption maximum of the 2,4-dinitrophenylhydrazone at 357 mμ indicates that the carbonyl group is unconjugated.[10] Of the positions possible for the olefinic link, only one is compatible with the proton magnetic resonance behavior of the unsaturated acid. The signals due to vinylic and carboxylic hydrogens readily were identified and the areas enclosed by the peaks were found to be equal, thereby indicating the presence of *one* vinylic hydrogen in the unsaturated acid molecule. The Δ^4- and Δ^5-positions for the double bond are thus excluded, and the proposed structure XXI for the unsaturated aldehyde is justified in detail.

The possibility of generating the 7-camphenyl carbonium ion by solvolysis of 7-camphenyl tosylates also was investigated. β-Isocamphor provided a crystalline tosylate (XXIV), the structure of which was confirmed by lithium aluminum hydride reduction to β-isocamphor. Solvolysis carried out at 140° in acetic acid–acetic anhydride–potassium acetate gave rise to material which was presumed to be the acetate of β-isocamphor, since

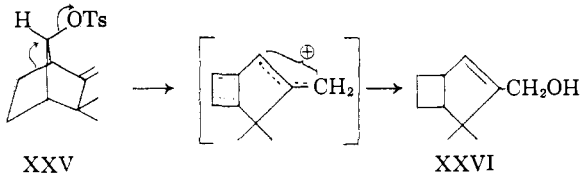
(7) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).

(8) (a) W. Klein, "Progress in Stereochemistry," Academic Press, Inc., New York, N. Y., 1954, p. 79 (and references cited therein); (b) W. G. Dauben, G. J. Fonken and D. S. Noyce, THIS JOURNAL, **78**, 2579 (1956).

(9) R. N. Chakravarti, *J. Indian Chem. Soc.*, **20**, 307 (1943); *J. Chem. Soc.*, 1565 (1947).

(10) E. A. Braude and E. R. H. Jones, *ibid.*, 498 (1945).

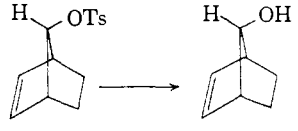
on hydrolysis this alcohol was formed as the only isolable product. Rearrangement prior to solvolysis was rendered unlikely by the observation that the tosylate was recovered in good yield after being heated for 16 hours in either refluxing aqueous alkali or a refluxing solution of sodium thiophenoxide in isopropyl alcohol. The tosylate XXV obtained from *syn*-7-camphenol, although not studied in detail, behaved quite differently. Hydrolysis, carried out in aqueous bicarbonate at 200°, led to no detectable amount of either 7-camphenol, in that the bands in the infrared characteristic of the terminal methylene group were absent from the solvolysis product. Manganese dioxide oxidation, considered to be specific for allyl alcohols,[11] converted the product carbinol to a carbonyl compound, $C_{10}H_{14}O$, characterized as α,β-unsaturated by its ultraviolet absorption at 243 mμ[12] as well as that (λ_{max} 377 mμ) of the 2,4-dinitrophenylhydrazone.[10] Although the structure of the hydrolysis product was not proved rigorously, the evidence presented strongly suggests XXVI for the allyl



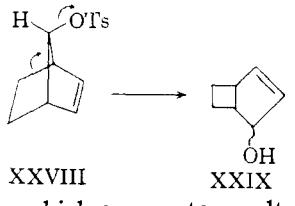
XXV XXVI

alcohol, formed by bond migration concomitant with production of an allyl carbonium ion.

Recent workers[13] have shown that *anti*-7-norbornenyl tosylate (XXVII) solvolyzes with retention of configuration; the *syn* isomer XXVIII, on the other hand, suffers ring contraction with formation of the bicyclo[3,2,0]heptenol (XXIX).



XXVII



XXVIII XXIX

Thus the products which appear to result from solvolyses of *syn*- and *anti*-7-camphenyl tosylates correspond to those derived from these simple analogs.

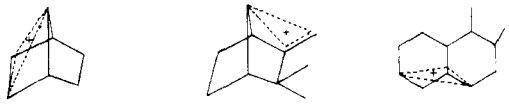
The acetolysis rates of the tosylates prepared from *anti*-7-camphenol, *syn*-7-camphenol and *syn*-7-isocamphanol were found to be first order and are listed in Table I, along with the rate of 7-norbornyl tosylate for comparison. Although data sufficient to permit a thorough and rigid analysis of the reaction systems were not sought, the interpretations presented below are considered to account, at least partially and in a qualitative way, for the observed solvolysis rates and products. It may be noted first of all that, as expected, the rates for *syn*-7-isocamphanyl- and 7-norbornyl tosylates fall in the same range, the greater value probably being due to steric acceleration by the *exo*-methyl group of the terpenoid tosylate. However, the derivatives of both the unsaturated alcohols solvolyze *more slowly* than the isocamphanyl ester, a finding at first glance surprising in view of the fact that the former are homoallyl derivatives. The *anti*-7-camphenyl case contrasts strikingly with the 7-norbornenyl example referred to above, where the solvolysis rate outweighs that of the norbornyl sulfonate by a factor of 10.[11] This spectacular difference has been ascribed[13,14] to the anchimeric assistance to the leaving group provided by the 2,3-π-electrons with formation of a symmetrical, highly stabilized homoallylic, or "bis-homocyclopropenyl,"[14] cation (XXX). Despite the fact

TABLE I

ACETOLYSIS RATES OF *p*-TOLUENESULFONATES AT 140 ± 1°[a]

	k 10³, hr.⁻¹	Relative k
anti-7-Camphenyl	4.6	6
syn-7-Camphenyl	11	13
syn-7-Isocamphanyl	15	18
7-Norbornyl	0.83[b]	1

[a] Carried out in anhydrous acetic acid containing 1% acetic anhydride and 0.1 *N* in potassium acetate. [b] This value was obtained by extrapolation using the values reported by Winstein (ref. 13) for the activation energy and rate constant at 205°.



XXX XXXI XXXII

that the 7-camphenyl case is not nearly as favorable for solvolysis, some rate enhancement over the saturated counterpart might have been anticipated; the non-classical homoallylic carbonium ion XXXI is more comparable to the cholesteryl carbocation XXXII, formation of which from cholesteryl-3-tosylate is associated with a rate increase of *ca.* 10^2 over cyclohexyl tosylate.[15] Certainly the very different nature of the products which result from the *syn*- and *anti*-7-camphenyl tosylates indicates that these reactants do not give rise to a common intermediate, but that the course of reaction is directed in each case by factors which must be reflected, to some degree at least, in the over-all rate. Although we have no direct evidence bearing on the point, it is possible that assistance by the double bond is operative, but is obscured by other effects. For example, on the basis of the observation that the double bond in 3-cyclopentenyl *p*-toluenesulfonate lowers, by comparison to the corresponding cyclopentyl case, the over-all rate of carbonium ion formation at C-1 by a factor of about 10,[16] the π-electron cloud in the 7-cam-

(11) F. Sondheimer, C. Amendolla and G. Rosenkranz, THIS JOURNAL, **75**, 5930 (1953).

(12) Δ^1-Cyclopentenaldehydes absorb at markedly longer wave lengths than conjugated cyclohexene- or acyclic aldehydes (W. M. Shubert and W. A. Sweeny, *ibid.*, **77**, 2298 (1955)).

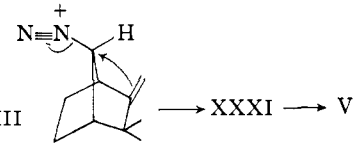
(13) (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); (b) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(14) W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(15) S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948).

(16) Personal communication from Prof. Winstein and J. Sonnenberg.

phenyl tosylate would be expected to diminish measurably the over-all solvolysis rate. Apart from these considerations, the 7-camphenyl homoallylic carbonium ion may not enjoy the same degree of stability as, *e.g.*, the cholesteryl system XXXII, because (1) geometrical factors may not be as favorable for π-orbital overlap and (2) the degree of alkyl substitution in the non-classical ion is not as high. Since camphenamine is also an *anti* isomer, reaction of the derived diazonium salt XXXIII to give alcohol with retention of configuration may also involve non-classical contributions of the homoallylic type.



XXXIII ⟶ XXXI ⟶ V

The solvolysis rate constant of *syn*-7-norbornenyl tosylate is 10^4 times greater than that of 7-norbornyl tosylate,[13] and this difference has been attributed to methylene participation with formation of the allylic cation XXXIV. On the basis of prod-

XXXIV

uct analysis, similar factors must be operative in the acetolysis of *syn*-7-camphenyl tosylate; these factors are, again, not apparent from the value of the rate constant. Although the contributory effects are difficult to evaluate, the shielding effect of π-electrons again may have reduced substantially the reaction rate. Also, the allyl carbonium ion—primary-secondary and unsymmetrical—originating from the camphenyl tosylate would not be as stable as the one arising in the norbornenyl tosylate solvolysis, and may assist in reducing the over-all solvolysis rate to a deceptively low value.

Acknowledgment.—The authors are grateful to Prof. Paul Bender for providing and interpreting n.m.r. data, and to Mr. Wilmer Miller for deuterium analyses.

Experimental[17]

β-Aminoborneol from Lithium Aluminum Hydride Reduction of α-Aminocamphor.—A solution of α-aminocamphor (crude product obtained by reduction of 20 g. (0.11 mole) of isonitrosocamphor) in 200 cc. of anhydrous ether was added to a suspension of 4.3 g. of lithium aluminum hydride in 600 cc. of anhydrous ether over a period of one hour, and the mixture allowed to stir overnight. The excess lithium aluminum hydride was decomposed by the dropwise addition of water while stirring vigorously. In rapid succession 6.0 cc. of water, 6.8 cc. of 10% sodium hydroxide and 10 cc. of water were added. The ether solution was decanted from the precipitated salts, and the salts were washed several times with fresh portions of ether. After drying over anhydrous sodium carbonate, the ether was removed under reduced pressure leaving a white solid which on crystallization from ligroin (60–68°) afforded 12.6 g. (67.5%) of β-aminoborneol, m.p. 172–173°.

α-Aminoborneol from Catalytic Reduction of α-Aminocamphor.—A solution of 8 g. (0.044 mole) of freshly prepared α-aminocamphor in 20 cc. of dry xylene was stirred for a short time with 3 g. of W-1 Raney nickel. The nickel was removed by filtration, 0.8 g. of platinum oxide added and the hydrogenation performed under 2 atm. of hydrogen at room temperature. The reaction consumed 71% of the calculated amount of hydrogen in 48 hr. After removal of the catalyst by filtration, the reaction mixture was subjected to steam distillation until no more xylene could be detected in the distillate. The aqueous residue remaining was extracted with three 100-cc. portions of ether and the combined ether extracts dried over anhydrous sodium carbonate. The ether was concentrated to a volume of 50 cc. and the aminoborneol allowed to crystallize. Filtration afforded 4.0 g. (49.4%) of crystalline α-aminoborneol which when recrystallized from ligroin (60–68°) had m.p. 189.8–191.8°.

β-Isocamphor (*anti*-7-Hydroxycamphene).—The directions outlined by Duden[2] afforded the alcohol in about 50% yield. It was found that in some cases the diazotization reaction was very slow and that the addition of a few drops of 10% sulfuric acid greatly facilitated the rate.

Dihydro-β-isocamphor (*anti*-7-Hydroxyisocamphane) (VI).—A solution of 300 mg. (1.97 moles) of β-isocamphor in 10 cc. of absolute ethanol containing 40 mg. of 10% palladium-on-carbon was hydrogenated at atmospheric pressure. Of a calculated 60 cc. of hydrogen, 54 cc. was consumed in less than 0.5 hour. The catalyst was removed by filtration and the ethanol removed under reduced pressure. The remaining oil was sublimed at 80° (15 mm.), yielding 250 mg. (82.4%) of the saturated alcohol, m.p. 92–93.5°. Several more sublimations afforded an analytical sample, m.p. 97–98°, $[\alpha]^{24}D$ −2.82° (*c* 2.43 in methanol).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.63; H, 11.73.

7-Ketoisocamphane (VII).—To a solution of 1.068 g. of chromium trioxide in 10 cc. of pyridine was added a solution of 400 mg. (2.6 mmoles) of dihydro-β-isocamphor (VI) in 4 cc. of pyridine and the resulting mixture stirred magnetically for 24 hours. Water (28 cc.) was added and the solution extracted with three 60-cc. portions of ether. The combined ether extracts were washed with water, 5% hydrochloric acid, and finally with water. After drying over anhydrous sodium carbonate, the ether was removed by distillation and the resulting oil sublimed at 80° (15 mm.), yielding 354 mg. (89.5%) of the crystalline ketone, m.p. 84–88°.

A portion of this material was converted to the 2,4-dinitrophenylhydrazone in the usual manner. After several recrystallizations from aqueous ethanol an analytical sample was obtained, m.p. 132–132.5°. The infrared absorption spectrum of VII exhibited strong absorption at 5.7 μ indicative of a bridged carbonyl.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 57.79; H, 5.92.

Isocamphane (IX) from 7-Ketoisocamphane (VII).—Boron trifluoride etherate (0.4 cc.) was added to a solution of 152 mg. (1 mmole) of 7-ketoisocamphane (VII) in 0.4 cc. of ethanedithiol and the mixture allowed to stand for 1 hour at room temperature. The mixture then was transferred to a separatory funnel with the aid of a few cc. of acetic acid, diluted with water and extracted with 30 cc. of ether in three portions. The combined ether extracts were washed with 5% sodium hydroxide solution and then with water. The ether was removed by distillation and the resulting oil dissolved in 10 cc. of absolute ethanol. Raney nickel (*ca.* 3 g.) was added and the mixture refluxed for 1 hour. The nickel was removed by filtration and washed with several cc. of ethanol. The alcohol solution was diluted with 100 cc. of water and extracted with three 15-cc. portions of ether. The ether extracts were washed with water and the ether removed by distillation. Attempts to crystallize the product directly failed, but sublimation at 68° (20 mm.) yielded 32 mg. (23.5%) of a characteristically partially crystalline solid, m.p. 55–60°. Melting point and infrared spectra (as solid film) comparison with an authentic sample of IX (m.p. 57–59°) served to establish the identity of this hydrocarbon.

Deuterium Exchange of 7-Ketoisocamphane (VII).—Sodium (*ca.* 80 mg.) was dissolved in 4 cc. of deuteroethanol and to this solution was added 87 mg. (0.58 mmole) of the ketone VII. After allowing the solution to stand 24 hours at room temperature, 2 cc. of deuterium oxide was added and the solution extracted with ether. The ether

(17) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were recorded on a Baird automatic recording spectrophotometer and unless otherwise specified were measured on chloroform solutions. The ultraviolet spectra were recorded on a Cary recording spectrophotometer using 95% ethanol as solvent.

extracts were washed first with 2 cc. of deuterium oxide and then with water. After drying over anhydrous sodium sulfate, the ether was removed by distillation and the resulting product sublimed at 75° (20 mm.), yielding 53 mg. (61%) of the starting ketone. A sample was converted to the 2,4-dinitrophenylhydrazone derivative, m.p. 130–131°, which served to establish the identity of the product.

A sample of the recovered ketone was submitted for deuterium analysis and was found to contain the normal abundance of deuterium (0.012 ± 0.002 atom per cent.).

β-Isocamphor *p*-Toluenesulfonate (*anti*-7-Camphenol *p*-Toluenesulfonate) (XXIV).—To a solution of 764 mg. (4 mmoles) of *p*-toluenesulfonyl chloride in 2 cc. of anhydrous pyridine (previously cooled to 0°) was added 304 mg. (2 mmoles) of β-isocamphor (Va). After allowing the solution to stand 24 hours at room temperature, water was added dropwise until about 1 cc. had been added. The solution then was diluted with about 50 cc. of water and extracted with three 50-cc. portions of ether. The combined ether extracts were washed with water, 5% hydrochloric acid, 5% sodium hydroxide and water. After drying over anhydrous sodium carbonate, the ether was removed by distillation yielding 598 mg. (98%) of a slightly colored oil, which crystallized on seeding, m.p. 50–52°. Several recrystallizations from ligroin (60–68°) at Dry Ice–acetone temperatures afforded an analytical sample, m.p. 53.1–53.6°. The ultraviolet absorption spectrum of XII exhibited λ_{max} 225 mμ (ε 13,800).

Anal. Calcd. for $C_{16}H_{22}O_3S$: C, 66.65; H, 7.24. Found: C, 66.67; H, 6.98.

Attempts to Replace the Tosyloxy Group of β-Isocamphor *p*-Toluenesulfonate (XII).—The results of these attempted replacements are summarized in the following table. In each case the only identifiable product was the starting *p*-toluenesulfonate.

Replacing group	Base	Solvent and conditions	Recov. starting material, %
HO–	NaOH	H_2O, reflux 16 hr.	100
$C_6H_5CH_2S$–	6 *N* NaOH	H_2O, reflux 6 hr.	96
C_6H_5S–	1 mole NaOEt	EtOH, reflux 2 hr. then room temp. 12 hr.	86
C_6H_5S–	1 mole sodium isopropoxide	Isopropyl alcohol, reflux 16 hr.	96

β-Isocamphor (Va) from Lithium Aluminum Hydride Cleavage of β-Isocamphor *p*-Toluenesulfonate (XXIV).—A solution of 187 mg. (0.6 mmole) of the ester in 10 cc. of anhydrous ether was added to a slurry of 23 mg. of lithium aluminum hydride in 50 cc. of anhydrous ether. After stirring for 28 hours, the excess lithium aluminum hydride was decomposed by the careful addition of water. The dropwise addition of 10% sodium hydroxide caused the precipitated salts to coagulate. The ether was removed by decantation and the salts washed with several fresh portions of ether. After drying the ether extracts over anhydrous sodium carbonate, the ether was removed by distillation and the resulting oil subjected to sublimation at 80° under reduced pressure. A white crystalline solid separated which after recrystallization from ligroin (60–68°) had m.p. 99.4–100.6°. No depression was observed in the melting point of this material on admixture with pure β-isocamphor.

7-Ketocamphene (XI).—To the complex prepared by adding 400 mg. of chromic acid to 4 cc. of pyridine was added a solution of 152 mg. (1 mmole) of β-isocamphor in 1 cc. of pyridine. The resulting mixture was stirred for 23 hours. At the end of this time 14 cc. of water was added and the solution extracted with 120 cc. of ether in three portions. The ether extracts were washed with water, 5% hydrochloric acid, 5% sodium hydroxide, and water. After drying over anhydrous sodium carbonate, the ether was removed by careful distillation, with the last traces being removed under reduced pressure. Sublimation of the residual oil at 80° (atmospheric pressure) afforded 103 mg (68.6%) of a partially crystalline solid, m.p. 55–66° (sealed tube).

A sample of the ketone was converted to the 2,4-dinitrophenylhydrazone. Several recrystallizations from aqueous ethanol afforded an analytical sample, m.p. 126–127°.

Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49. Found: C, 58.53; H, 5.65.

The infrared absorption spectrum of XX in chloroform exhibited maxima at 5.70 μ indicative of a bridged carbonyl and at 6.03 and 11.3 indicative of a terminal methylene.

***syn*-7-Hydroxycamphene (XII).**—A solution of 244 mg. (1.63 mmoles) of 7-ketocamphene in 2 cc. of methanol was added to a solution of 300 mg. of sodium borohydride in 5 cc. of water containing 2 cc. of methanol and the mixture allowed to stand overnight at room temperature. At the end of this time 10 cc. of a 5% sodium hydroxide solution was added and the mixture stirred for 0.5 hours. The solution was extracted with three 15-cc. portions of ether and the combined extracts dried over anhydrous sodium carbonate. The ether was removed by distillation and the resulting solid sublimed at 90° (15 mm.) yielding 200 mg. (80.8%) of the alcohol, m.p. 115–118°. Several recrystallizations from ligroin (60–68°) at Dry Ice–acetone temperature and sublimation afforded an analytical sample, m.p. 120.6–121.8°, $[\alpha]^{24}D$ +52.5° (*c* 2.43, in methanol).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.47; H, 10.80.

This compound exhibited characteristic absorption bands in the infrared at 6.03 and 11.3 μ (terminal methylene). The entire spectrum was similar to that of β-isocamphor. The most striking difference was the appearance of two small bands at 10.28 and 10.85 μ which were not present in the spectrum of β-isocamphor.

***syn*-7-Hydroxyisocamphane (XVII) from Sodium Borohydride Reduction of 7-Ketoisocamphane.**—The procedure used for the preparation of this compound was exactly the same as that described above for the preparation of *syn*-7-hydroxycamphene. A 200-mg. sample (1.32 mmoles) of the ketone VII yielded 195 mg. (96%) of the crude crystalline alcohol, m.p. 119–121.6°. Several additional sublimations at 80° (10 mm.) afforded an analytical sample, m.p. 121.4–122.5°, $[\alpha]^{24}D$ −36.0° (*c* 4.21, in methanol).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.11; H, 11.61.

***syn*-7-Hydroxyisocamphane (XVII) from Lithium Aluminum Hydride Reduction of 7-Ketoisocamphane.**—To a slurry of 300 mg. of lithium aluminum hydride in 15 cc. of anhydrous ether was added a solution of 7-ketoisocamphane in 5 cc. of anhydrous ether. After stirring for 18 hours, the excess lithium aluminum hydride was decomposed by the careful addition of water and in rapid succession 0.6 cc. of water, 1.4 cc. of 5% sodium hydroxide and 0.5 cc. of water were added. The ether was decanted from the precipitated salts and the salts were washed with several fresh portions of ether. After drying the combined extracts over anhydrous sodium carbonate, the ether was removed by distillation. The product was isolated by sublimation yielding 141 mg. (92.8%) of the *syn*-alcohol XVII, m.p. 120.4–121.6°.

***syn*-7-Hydroxyisocamphane (XVII) from Catalytic Reduction of 7-Ketoisocamphane in Acid Solution.**—One hundred mg. of platinum oxide was suspended in 10 cc. of acetic acid containing 2 drops of hydrochloric acid and reduced to platinum metal with hydrogen at atmospheric pressure. A solution of 150 mg. (0.986 mmole) of 7-ketoisocamphane was added and the solution treated with hydrogen at room temperature at atmospheric pressure. In 2 hours 25.9 cc. of gas was consumed (calcd. for 1 equivalent, 25.0 cc.). The catalyst was removed by filtration, the solution diluted with 75 cc. of water and extracted with three 25-cc. portions of ether. After drying over anhydrous sodium carbonate, the ether was removed by distillation and the resulting oil evaporatively distilled at 68° (15 mm.), yielding 151 mg. (78.5%) of the acetate as a colorless liquid. The infrared absorption spectrum served to establish that acetylation had occurred.

The acetate (151 mg.) was saponified with 5 cc. of 5% aqueous sodium hydroxide to which was added a small amount of Dreft. After refluxing for 3 hours, the mixture was extracted with ether. The ether extracts were dried over anhydrous sodium sulfate and the ether removed by distillation. Sublimation of the resulting oil afforded 58 mg. (49.3% based on acetate) of the *syn*-alcohol XVII, m.p. 118.5–121.5°, as the only volatile product.

β-Isocamphor from Sodium and Alcohol Reduction of 7-Ketocamphene.—To a solution of 36 mg. (0.24 mmole) of the ketone XI in 4 cc. of absolute ethanol was added 230 mg. of sodium in small pieces and the mixture refluxed until all the sodium had reacted. The solution was diluted to 40 cc. with water and extracted with three 15-cc. portions

of ether. After drying over anhydrous sodium carbonate, the ether was removed by distillation leaving a brown oil which crystallized on scratching. Sublimation at 80° (12 mm.) yielded 25 mg. (67.6%) of the crystalline alcohol, m.p. 85–90°. Mixed melting point comparison (m.p. 86–98°) with authentic Va (m.p. 100–101°) indicated that this isomer predominated in the mixture. The infrared spectrum was essentially identical with that of Va and more important it exhibited no absorption bands at 10.28 and 10.85 μ which are characteristic of the *syn* isomer.

***syn*-7-Camphenol *p*-Toluenesulfonate (XXV)** was prepared from *syn*-7-hydroxycamphene by reaction with *p*-toluenesulfonyl chloride in pyridine following the exact procedure described above for the preparation of β-isocamphor *p*-toluenesulfonate.

From 304 mg. (2 mmoles) of the alcohol there was obtained 581 mg. (95%) of the desired ester, m.p. 79–80°. Several recrystallizations from ligroin (60–68°) at Dry Ice–acetone temperature afforded an analytical sample, m.p. 85.4–86°. The ultraviolet absorption spectrum of XXXV exhibited λ_{max} 225 (ε 11,700).

Anal. Calcd. for $C_{17}H_{22}O_3S$: C, 66.65; H, 7.24. Found: C, 66.48; H, 7.47.

***syn*-7-Isocamphanol *p*-toluenesulfonate** was prepared from *syn*-7-hydroxyisocamphane by reaction with *p*-toluenesulfonyl chloride in pyridine following the exact procedure described above for the preparation of β-isocamphor *p*-toluenesulfonate.

From 194 mg. of the alcohol there was obtained 387 mg. (96%) of the ester, m.p. 52–59°. Several recrystallizations from ligroin (60–68°) at Dry Ice–acetone temperatures afforded an analytical sample, m.p. 65.5–67.4°.

Anal. Calcd. for $C_{17}H_{24}O_3S$: C, 66.21; H, 7.85. Found: C, 66.61; H, 7.84.

Determination of the Rate Constants.—The technique employed was essentially that of Winstein.[18] The constant temperature bath was a converted Dry Ice condenser in which ethylene glycol was heated by refluxing xylene. The temperature control was 140 ± 1°. The acetolyses were conducted in sealed tubes containing 3 or 5 cc. of sample which were removed from the bath at the specified times and 1- or 2-cc. aliquots titrated with the standard acid solution using a saturated solution of brom cresol blue in acetic acid as indicator.

Allyl Alcohol (XXVI) from the Acetolysis of *syn*-7-Camphenol *p*-Toluenesulfonate.—The combined titration residues were diluted with 100 cc. of water and extracted with three 100-cc. portions of ligroin (40–42°). The combined extracts were washed with water, filtered through anhydrous sodium carbonate and the ligroin removed by distillation. The resulting colored oil was refluxed with 10 cc. of aqueous 10% sodium hydroxide for 3 hours. Extraction with ether yielded a brown oil which was evaporatively distilled at 78° (15 mm.) affording 71 mg. of a colorless liquid. The infrared absorption spectrum of this material exhibited little similarity to that of *syn*-7-hydroxycamphene. An absorption band at 2.95 μ indicated the presence of an hydroxyl group but the spectrum lacked the familiar bands at 6.03 and 11.3 μ which characterize the terminal methylene of the camphene nucleus.

β-Isocamphor from the Acetolysis of β-Isocamphor *p*-Toluenesulfonate.—The combined titration residues were diluted with 100 cc. of water and extracted with three 50-cc. portions of ligroin (40–42°). The combined extracts were washed with water and the ligroin removed by distillation. The residual brown-colored oil was refluxed for 1 hr. in 7 cc. of aqueous 10% sodium hydroxide. The mixture was diluted with 20 cc. of water and extracted with ether. The ether extracts were washed with water and filtered through anhydrous sodium carbonate. Removal of the ether by distillation and then sublimation at 80° (15 mm.) afforded β-isocamphor m.p. 94–98°. No depression was observed on mix-melting with authentic material.

Allyl Alcohol (XXVI) from the Solvolysis of *syn*-7-Camphenol *p*-Toluenesulfonate in Aqueous Sodium Bicarbonate.—A mixture of 80 mg. (0.0262 mmole) of the *p*-toluenesulfonate ester XXV and 5 cc. of 0.2 *N* aqueous sodium bicarbonate was placed in a sealed tube and heated at 200° for 5 days. The mixture was extracted with three 10-cc. portions of ether and the combined extracts washed with water. After filtering through anhydrous sodium carbonate, the ether was removed by distillation yielding 34 mg. of brown oil. Evaporative distillation of this material at 80° (15 mm.) afforded 26 mg. (65.4%) of the impure allyl alcohol. To a solution of 26 mg. of the crude alcohol in 3 cc. of chloroform was added 260 mg. of manganese dioxide. The mixture was stirred for 1.5 hours at room temperature. The solids were removed by filtration and washed with several portions of ether. Removal of the solvents by distillation afforded 16 mg. of a camphoraceous smelling oil. This crude material absorbed strongly in the ultraviolet at 243 μ.

A 10-mg. sample of the crude ketone was converted to the 2,4-dinitrophenylhydrazone affording 9 mg. of the derivative, m.p. 162–164°. The ultraviolet absorption spectrum exhibited λ_{max} 377 μ (ε 27,000). Several recrystallizations from aqueous ethanol afforded an analytical sample m.p. 166.6–168.4°.

Anal. Calcd. for $C_{16}H_{16}O_4N_4$: C, 58.17; H, 5.49. Found: C, 58.12; H, 5.50.

The same 2,4-dinitrophenylhydrazone was obtained from the oxidation of the alcohol resulting from the saponification of the acetolysis product.

2,2,3-Trimethyl-3-cyclohexene-1-carboxaldehyde 2,4-Dinitrophenylhydrazone (XIX) from β-Isocamphor.—To a solution of 25 mg. (0.165 mmole) of β-isocamphor in 1 cc. of 95% ethanol was added 0.8 cc. of 2 4-dinitrophenylhydrazine reagent. The solution was heated to boiling on the steam-bath and then allowed to stand 36 hours at room temperature. The yellow solid (20.7 mg.) was separated by centrifugation. Treatment of the mother liquors with several more drops of the 2,4-dinitrophenylhydrazine reagent afforded an additional 16 mg. of the derivative. The total yield was 36.7 mg. (67.2%), m.p. 130–140°. The ultraviolet absorption spectrum exhibited λ_{max} 357 mμ. Several recrystallizations from aqueous ethanol afforded an analytical sample, m.p. 153.8–154.2°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 57.80; H, 5.94.

2,2,3-Trimethyl-3-cyclohexene-1-carboxaldehyde (XXI) from β-Isocamphor.—To 3 cc. of a solution prepared by mixing 3 cc. of water, 2 cc. of concentrated sulfuric acid and 12 cc. of 95% ethanol was added 152 mg. (1 mmole) of β-isocamphor. The solution was allowed to stand at room temperature for 2 days after which it was refluxed for 30 minutes on the steam-bath. The hot solution was poured into 50 cc. of ice-water and extracted with ether. The ether extracts were washed with water and dried over anhydrous sodium carbonate. Removal of the ether by distillation afforded 127 mg. of the crude aldehyde. The infrared spectrum exhibited absorption bands at 6.1, 11.3 and 2.95 μ which indicated the presence of some of the starting alcohol. Additional bands at 5.90 and 3.7 μ established the presence of the aldehyde function.

2,2,3-Trimethyl-3-cyclohexene-1-carboxylic Acid (XXII).—A 118-mg. sample of the crude aldehyde XXI was added to a solution of 264 mg. of silver nitrate in 1 cc. of water and enough ethanol was added to make the solution homogeneous. A solution of 124 mg. of sodium hydroxide in 1 cc. of water was added and the mixture stirred for 1 hour. The precipitated silver was removed by filtration and washed with several cc. of water. The filtrate was extracted with ether until the ether extracts were no longer colored. The last traces of ether were removed from the aqueous solution with a gentle stream of nitrogen. When the solution was cooled in an ice-bath and carefully acidified with concentrated hydrochloric acid, a yellow crystalline acid precipitated. The compound was separated by filtration and dried in a vacuum desiccator. The crude acid thus obtained weighed 78 mg. and had m.p. 74–75°. After treatment with Norite in ethanol, recrystallization from aqueous ethanol and sublimation at 75° (0.1 mm.), a white crystalline acid (22 mg.) was obtained, m.p. 77.6–78.6°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.64; H, 9.64.

The nuclear magnetic resonance spectrum of XXII in carbon tetrachloride was obtained and the area under the curve corresponding to vinyl hydrogen was found to be the same as the area under the curve corresponding to carboxyl hydrogen.

2,2,3-Trimethylcyclohexane-1-carboxylic Acid (XXIII) from the Catalytic Reduction of XXII.—A 8.35-mg. (0.0496 mmole) sample of the unsaturated acid XXII in 2 cc. of ab-

(18) S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, **70**, 812 (1948).

solute ethanol was hydrogenated over 3 mg. of 10% palladium-on-carbon at atmospheric pressure and room temperature. The measured volume of hydrogen consumed was 1.53 cc. (calcd. for 1 equivalent, 1.25 cc.). The catalyst was removed by centrifugation and washed with several portions of ether. Evaporation of the solvents yielded an oil which partially crystallized when scratched with a glass stirring rod. The product was dissolved in 1 cc. of methanol and sufficient water added to make the solution cloudy. Cooling in an ice-bath with scratching caused crystallization to occur. The crystalline acid was separated by centrifugation and had m.p. 53–56°. Sublimation at 75° (15 mm.) afforded 3.5 mg. (41.5%) of the pure acid, m.p. 55.5–57° (reported[9] 58°). Mixed melting point comparison with an authentic sample of XXIII (m.p. 52–55.5°) exhibited no depression.

The *p*-phenylphenacyl ester of XXIII was prepared and found to melt at 109–110° (reported[9] 114°).

MADISON 6, WIS.

[CONTRIBUTION FROM THE NATIONAL RESEARCH CENTER AND THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

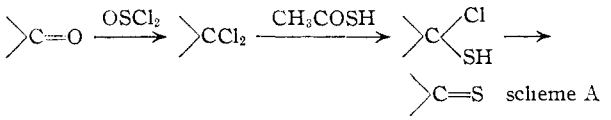
Experiments with 4-Thiopyrones and with 2,2′,6,6′-Tetraphenyl-4,4′-dipyrylene. The Piezochromism of Diflavylene

BY ALEXANDER SCHÖNBERG, MOHAMED ELKASCHEF, MICHAEL NOSSEIR AND MAHMOUD MOHAMED SIDKY

RECEIVED JUNE 2, 1958

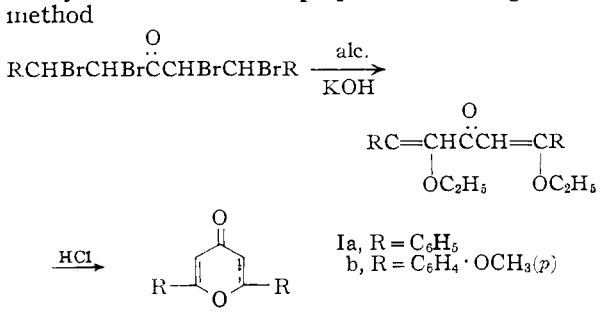
2,6-Diaryl-4-pyrones are transformed into the corresponding 4-thiopyrones by using the thioacetic acid method. The action of mercuric chloride and of diazomethane (comp. II → III) on these thioketones is described. Compound IIIa is transformed by the action of lithium phenyl into 2,2′,6,6′-tetraphenyl-4,4′-dipyrylene (XII), and 2,2′-distyryl-dichromylene from 2-styryl-4-thiochromone (comp. IVb → Vb → VIb) is obtained by a similar process. The action of diphenyldiazomethane (and of 9-diazofluorene) on 2,6-diphenyl-4-thiopyrone yields the ethylene derivatives X (yellow) and XI (red), respectively. The lack of reactivity of 2,2′,6,6′-tetra-phenyl-4,4′-dipyrylene is explained by the application of the resonance theory (comp. XIIa → XIIb). A theory advanced to explain the piezochromic properties of diflavylene (VIa) by reversible *cis–trans* changes (XIVa ⇄ XIVb) cannot be accepted as similar properties are also shown by XV and XVI.

Synthesis of 4-Thiopyrone from γ-Pyrones by the Thionyl Chloride–Thioacetic Acid Method.—The transformation of ketones into the corresponding thioketones according to scheme A has been successfully carried out with benzophenones and xanthiones,[1] but not with γ-pyrones. We have succeeded in obtaining 2,6-diphenyl-4-thiopyrone (IIa) and 2,6-di-(*p*-methoxyphenyl)-4-thiopyrone (IIb) according to the scheme



scheme A

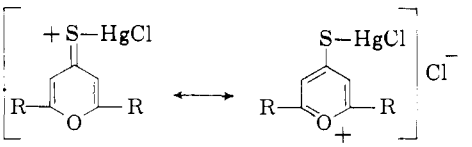
2,6-Di-(*p*-methoxyphenyl)-4-pyrone (Ib) used in the synthesis of IIb was prepared according to the method



Ia, R = C_6H_5
b, R = $C_6H_4 \cdot OCH_3(p)$

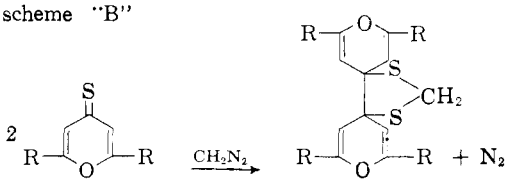
Compound IIa was obtained previously by Arndt, *et al.*,[2] by the action of phosphorus pentasulfide on Ia.

Reactions of 2,6-Diaryl-4-thiopyrones and 2-Styryl-4-thiochromones. (a) Color Reactions with Mercuric Chloride.—When mercuric chloride was added to a benzene solution of 2,6-diphenyl-4-thiopyrone (IIa), the colorless crystals acquired a yellow color[3] after a short time. With 2,6-di-(*p*-methoxyphenyl)-4-thiopyrone (IIb) the color was orange. The color reaction probably is due to the formation of compounds of the type



(b) Reactions with Diazomethane.—Nothing appears to be known about the action of diazomethane on 4-thiopyrones. We have found that the reaction with 2,6-diphenyl-4-thiopyrone (IIa) proceeds according to scheme B.

scheme "B"



IIa, R = C_6H_5
b, R = $C_6H_4 \cdot OCH_3(p)$

IIIa, R = C_6H_5

Similar reactions have been observed previously with 4-thioflavone (IVa)[4] and were now observed with the 2-styryl-4-thiochromones IVb, c and VIIa,b respectively.

2-Styrylchromone (the oxygen analog of IVb) was recovered unchanged when treated with diazomethane under the conditions leading to the formation of Vb and IVb.

(c) Reactions with Diphenyldiazomethane and Diazofluorene.—The action of diaryldiazomethane

(1) A. Schönberg, O. Schütz and S. Nickel, *Ber.*, **61**, 1375 (1928).
(2) F. Arndt, E. Scholz and P. Nachtwey, *ibid.*, **57**, 1903 (1924).
(3) A. Schönberg, *ibid.*, **58**, 1793 (1925); comp. A. Schönberg in Houben-Weyl, "Methoden der Organischen Chemie," Vol. 9, 1955, pp. 704–739.
(4) A. Schönberg and S. Nickel, *Ber.*, **64**, 2323 (1931).