6-Ethoxybenzothiophene-2-carboxaldehyde (IIIb). Two grams (0.011 mole) of 6-ethoxybenzothiophene, 2.0 g. (0.026 mole) of dimethylformamide and 3.0 g. of phosphorus oxychloride were dissolved in 10 ml. of dioxane and allowed to stand at room temperature for 2 hr. The mixture was heated at 70° for 3 hr. and poured into an aqueous solution of excess sodium acetate. After the mixture had been allowed to stand overnight, the precipitate was collected and recrystallized from dilute ethanol to give 0.8 g. (34%) of light straw-colored needles melting at 99°.

Anal. Calcd. for $C_{11}H_{10}O_2S$: S, 15.52. Found: S, 15.44.

6-Ethoxybenzothiophene-2-carboxaldehyde oxime. This derivative was found to melt at 171°.

Anal. Calcd. for $C_{11}H_{11}NO_2S$: S, 14.47. Found: S, 14.39.

Oxidation of the formyl derivative of 6-ethoxybenzothiophene. A 0.1-g. portion (0.0003 mole) of the aldehyde (IIIb) was added to a suspension formed by mixing 0.8 g. of silver nitrate and 0.5 g. of sodium hydroxide in 15 ml. of water. The mixture was heated on the steam bath for 1 hr. and filtered. The filtrate was acidified and the precipitate was recrystallized from ethanol to give 70 mg. (70%) of colorless needles melting at 221°. A mixed melting point with the acid obtained from the bromo derivative was not depressed, and their infrared spectra were identical.

6-Ethoxy-2-benzothienyl methyl ketone (IIIc). One gram (0.0056 mole) of 6-ethoxybenzothiophene (II) and 0.60 g. (0.0059 mole) of acetic anhydride were dissolved in 25 ml. of chloroform and 5 ml. of anhydrous stannic chloride was added. The green solution was warmed at 60° for 0.5 hr. after which 40 ml. of 10% hydrochloric acid was added and the mixture was boiled to decompose the complex. The organic layer was separated and evaporated to dryness to afford tan crystals which were recrystallized from 95% ethanol to give 1.0 g. (80%) of flat colorless needles melting at 107–108°.

Anal. Calcd. for $C_{12}H_{12}O_2S$: S, 14.53. Found: S, 14.47.

6-Ethoxy-2-benzothienyl methyl ketone oxime. This derivative melted at 178–179°.

Anal. Calcd. for $C_{12}H_{13}NO_2S$: S, 13.61. Found: S, 13.70.

Haloform oxidation of 6-ethoxy-2-benzothienyl methyl ketone. One-tenth gram of the ketone (IIIc) was refluxed 1 hr. with 1 g. of iodine, 5 ml. of dioxane, and 10 ml. of 10% sodium hydroxide solution. The reaction mixture was diluted with water, filtered, and acidified. The excess iodine was destroyed with 5% sodium bisulfite. The precipitate was collected and recrystallized from aqueous ethanol to give 40 mg. (40%) of white needles melting at 220–221°. A mixed melting point with the product obtained from the bromo derivative was not depressed, and their infrared spectra were identical.

5-(p-Ethoxybenzylidene)rhodanine. Five grams (0.033 mole) of *p*-ethoxybenzaldehyde (Aldrich Chemical Co.) was condensed with 5 g. of rhodanine in 40 ml. of glacial acetic acid using 10 g. of fused sodium acetate as catalyst, according to the method of Julian and Sturgis.[13] Isolation in the prescribed manner gave 8 g. (91%) of rhodanine derivative which was recrystallized from ethanol as yellow needles melting at 225–226°.

Anal. Calcd. for $C_{12}H_{11}NO_2S_2$: S, 24.15. Found: S, 24.19.

β-(p-Ethoxyphenyl)-α-mercaptoacrylic acid (VI). Eight grams (0.019 mole) of 5-(*p*-ethoxybenzylidene)rhodanine was hydrolyzed in 100 ml. of 10% sodium hydroxide on the steam bath for 0.5 hr. Isolation as described in reference 13 and recrystallization from acetone-ethanol gave 5 g. (62%) of orange prisms melting at 181–183° with gas evolution.

Anal. Calcd. for $C_{11}H_{12}O_3S$: S, 14.30. Found: S, 14.35.

Desulfurization of β-(p-ethoxyphenyl)-α-mercaptoacrylic acid. The procedure was the same as for desulfurization of 6-ethoxybenzothiophene-2-carboxylic acid above. One gram of the mercaptoacrylic acid was dissolved in 30 ml. of 10% sodium hydroxide solution and 10 ml. of water and treated with 4 g. of Raney nickel alloy. Workup as described above and several recrystallizations from aqueous ethanol gave 0.45 g. (55%) of colorless needles melting at 102°. A mixed melting point with the product obtained from IV was 102–103° (not depressed), and their infrared spectra were identical.

BLOOMINGTON, IND.

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(13) P. L. Julian and B. M. Sturgis, *J. Am. Chem. Soc.*, 57, 1126 (1935).

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

The Addition of *p*-Thiocresol to Two Conjugated Dienes

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Free-radical addition of *p*-thiocresol to 3-methylenecyclohexene (II) and to 1,2-dimethylenecyclohexane (I) led solely to the 1,4-addition products 1-cyclohexenylmethyl *p*-tolyl thioether (V) and 2-methyl-1-cyclohexenylmethyl *p*-tolyl thioether (III), respectively, no detectable amounts of the 1,2-addition products being formed. Comparison samples of the thioethers were prepared by alternative syntheses involving displacement reactions, as were the isomeric thioethers, 3-cyclohexenylmethyl *p*-tolyl thioether (VI) and 2-methylenecyclohexylmethyl *p*-tolyl thioether (IV); these isomers would have been formed had 1,2-addition obtained.

Free-radical addition of *p*-thiocresol to butadiene gave a 1:1 addition product which appeared to be largely the 1,4-addition product, *trans*-crotyl *p*-tolyl thioether,[1] little or no 1,2-addition product being formed. In order to test whether 1,4-*vs.* 1,2- addition might be affected by the *cis* or *trans* nature of the final product (and thus possibly of the intermediate radical), we have studied the addition of thiocresol to 1,2-dimethylenecyclohexane (I) and to 3-methylenecyclohexene (II). Of the possible addition products to I, the 1,4-addition product III appeared to be formed exclusively, no 1,2-addition product (IV) being noted. Similarly addition to II led to V with no evidence for VI in the product, although infrared spectra of V and VI were too similar to be certain that no VI was present.

Samples of III–VI were prepared by straightforward syntheses. III was prepared by reaction

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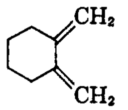
[1] J. A. Reeder, Ph.D. thesis, University of Colorado, 1958.



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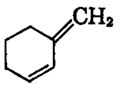

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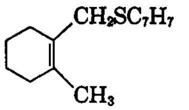

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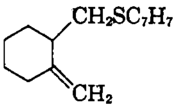

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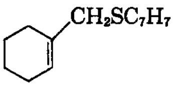
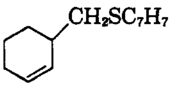
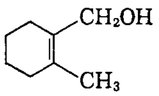


V



VI

of sodium thiocresoxide on the methanesulfonate of 2-methyl-1-cyclohexenylmethanol (VII),[2] while IV was prepared in a similar fashion from the alcohol VIII, the acetate of which[3] was the starting material. The sample of IV had three strong absorption peaks at 6.06 μ (1650 cm.$^{-1}$), 10.50–10.60 μ (942–952 cm.$^{-1}$) and 11.25 μ (889 cm.$^{-1}$) not clearly observable in the spectrum of crude or redistilled samples of III prepared by addition of thiocresol to I. The first and third of these peaks have been ascribed to compounds of the type $R_1R_2C{=}CH_2$.[4] It is of interest that the samples of III prepared by synthesis from VII did show small peaks ascribable to IV. This suggests that the synthesis of VII by hydroxymethylation of 1-methylcyclohexene[2] leads to a small amount of the isomer VIII. Both samples of III had small absorption peaks at 5.98 μ (1672 cm.$^{-1}$) characteristic[4] of a tetrasubstituted carbon-carbon double bond. This appeared to be absent in the sample of IV but its intensity was too small in pure III to be certain of this.



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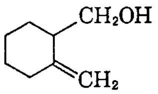

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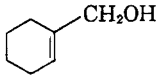
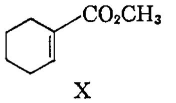
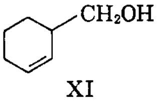


IX



X



XI

The two preparations of III were methylated to the sulfonium compounds with methyl sulfate and then converted to chloroplatinate derivatives. These were identical in melting point, mixed melting point and infrared spectra.

Compound V was prepared by treatment of the methanesulfonate of 1-cyclohexenylmethanol (IX) with sodium thiocresoxide. The alcohol IX was prepared by lithium aluminum hydride-reduction of the ester X.[5] Thioether VI was prepared from the methanesulfonate of XI, which was available by hydroxymethylation of cyclohexene.[6] Infrared spectra of V and VI had small differences; in particular that of samples of V had a peak at 10.85 μ (922 cm.$^{-1}$), absent in VI, while that of VI had peaks at 10.50 μ (952 cm.$^{-1}$) and 11.07 μ (903 cm.$^{-1}$) absent from V. These peaks were not strong, so deductions can not be firmly established. However, both samples of V were converted to identical palladous chloride samples while that of VI was different.

The results of these experiments show that 1,4-addition is favored over 1,2-addition whether or not the intermediate radical has *trans* or *cis* geometry.

The clean 1,4-addition of thiocresol to I is analogous with polymerization of I, which yields an all 1,4- highly crystalline polymer, with no evidence for terminal methylene groups.[7,8]

EXPERIMENTAL

All infrared spectra were run on a Perkin-Elmer Model 21C infrared spectrophotometer with compounds as films.

Addition of p-thiocresol to 1,2-dimethylenecyclohexane (I). *p*-Thiocresol (2.57 g., 0.0208 mole) was added slowly over a period of 15 min. to 2.25 g. (0.0208 mole) of 1,2-dimethylenecyclohexane (I).[3] The reaction mixture was stirred continuously with a micro thermometer. As the addition proceeded, the temperature of the reaction mixture rose to 71°. At this point the flask was cooled with water and the addition continued. After the addition was complete, the reaction mixture was heated on a steam bath for 50 min. Distillation gave 4.26 g. (88%) of 2-methyl-1-cyclohexenylmethyl *p*-tolyl thioether (III), b.p. 124–129° (0.15 mm.), n_D^{25} 1.5715. It was distilled again for the preparation of an analytical sample. The infrared spectrum is discussed above.

Anal. Calcd. for $C_{15}H_{20}S$: C, 77.58; H, 8.62; S, 13.79. Found: C, 77.56; H, 8.40; S, 13.79.

Methyl-2-methyl-1-cyclohexenylmethyl-p-tolylsulfonium acid chloroplatinate. The chloroplatinate was prepared by the method of Kehrmann and Duttenhofer.[9] One hundred milligrams of the thioether III was heated with 70 mg. of methyl sulfate in a small test tube at 100° for 5 hr. The reaction mixture was extracted with water; the aqueous solution was filtered and a solution of chloroplatinic acid was added to the clear filtrate. Upon concentration of the solution, yellowish-white crystals, which, when dry, weighed 141 mg., m.p. 175–177°, were obtained. Three crystallizations from hot water yielded an analytical sample, m.p. 181–182°.

Anal. Calcd. for $C_{16}H_{24}SPtCl_6$: C, 29.28; H, 3.66; Pt, 29.73. Found: C, 29.22; H, 3.66; Pt, 29.4, 28.5.

When mixed with the chloroplatinate obtained from synthetic III, m.p. 180–181.5°, it had m.p. 180–181.5° (see below).

2-Methyl-1-cyclohexenylmethanol (VII) was prepared according to the method of Nenitzescu and Przemetzky,[2] b.p. 100–104° (12 mm.), n_D^{25} 1.4877, (reported[2] b.p. 106–108° (20 mm.)). A mixture of 4 g. (0.0317 mole) of VII and 3.75 g. (0.0328 mole) of freshly distilled methanesulfonyl chloride

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(2) C. D. Nenitzescu and V. Przemetzky, *Ber.*, **74B**, 676 (1941).

(3) W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

(4) L. Bellamy, *The Infrared Spectra of Complex Molecules*, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 34–38.

(5) W. J. Bailey and R. A. Baylouny, *J. Am. Chem. Soc.*, **81**, 2126 (1959).

(6) I. N. Nazarov and N. V. Kuznetsov, *Doklady Acad. Nauk. S.S.S.R.*, **111**, 358 (1956).

(7) W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **76**, 5418 (1954).

(8) A. T. Blomquist and O. T. Longone, *J. Am. Chem. Soc.*, **79**, 3916 (1957).

(9) F. Kehrmann and A. Duttenhofer, *Ber.*, **38**, 4197 (1905).

was stirred in an ice salt bath. Dry pyridine, 12 ml., was added to the stirred mixture over a period of 1.5 hr. The stirring was continued for another 3 hr. The reaction mixture was poured into 75 ml. of ice-cold 10% hydrochloric acid. The resulting solution was extracted with two 50-ml. portions of ether. The ethereal solution was washed with water, with a saturated solution of sodium bicarbonate, and then dried over potassium carbonate. The ether was removed under reduced pressure. The crude methanesulfonate weighed 4.4 g. (69%). This was used as such for the preparation of III.

2-Methyl-1-cyclohexenylmethyl p-tolyl thioether (III). A solution of 381 mg. (0.0166 g.-atom) of sodium in 25 ml. of absolute ethanol was prepared, and 2.2 g. (0.0177 mole) of *p*-thiocresol was dissolved in this solution. The methanesulfonate of VII (3.4 g., 0.0166 mole) in 25 ml. of absolute ethanol was added to it. The mixture was allowed to stand at room temperature for 5 days, and was then poured into ice water. The aqueous solution was extracted with three 100-ml. portions of ether; the ethereal solution was washed successively with a dilute sodium hydroxide solution, water and a calcium chloride solution, then dried over calcium chloride. The ether was removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure to give 2.1 g. (55%) of III, b.p. 120–125° (0.25 mm.). It was chromatographed through activated alumina to remove any di-*p*-tolyl disulfide. Elution with petroleum ether (b.p. 60–70°) gave the pure product. It was distilled again to prepare an analytical sample, b.p. 120–126° (0.23 mm.), n^{25} 1.5745. The purity and infrared spectrum of this material are discussed above.

Anal. Calcd. for $C_{15}H_{20}S$: C, 77.58; H, 8.62; S, 13.79. Found: C, 77.60; H, 8.60; S, 14.06.

The acid chloroplatinate derivative of this thioether sample was prepared by the procedure described above starting with 50 mg. of the thioether. Sixty-eight milligrams of the product, m.p. 179.5–180.5°, was obtained. Two crystallizations from hot water gave a product which had m.p. 180–181.5°; the melting point was not depressed when this sample was admixed with the derivative prepared from the thioether III obtained from thiocresol and dimethylenecyclohexane (I).

2-Methylenecyclohexylmethanol (VIII). Seven and one-half grams (0.0446 mole) of 2-methylenecyclohexylmethyl acetate,[3] b.p. 88–90° (6 mm.), n_D^{25} 1.4634 [reported[3] b.p. 105–106° (20 mm.), n_D^{25} 1.4620], was heated at reflux with ethanolic sodium hydroxide solution for 1 hr. The ethanol was distilled under reduced pressure and the residue was poured into water. The organic layer was separated and the aqueous solution was extracted with ether. The combined organic solution was dried over anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under vacuum to give 3.77 g. (67%) of 2-methylenecyclohexylmethanol, b.p. 66–68° (2 mm.), n_D^{25} 1.4875.

Anal. Calcd. for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.46; H, 10.86.

2-Methylenecyclohexylmethyl p-tolyl thioether (IV). One and seven-tenths grams (0.0134 mole) of VIII was treated with an equivalent quantity of methanesulfonyl chloride in the presence of pyridine as above to give 1.3 g. (48%) of the crude methanesulfonate. This was treated with sodium *p*-thiocresoxide as described above to give 0.7 g. (50%) of IV, b.p. 104–112° (0.1 mm.), n_D^{25} 1.5618. The infrared spectrum is discussed above.

Anal. Calcd. for $C_{15}H_{20}S$: C, 77.58; H, 8.62; S, 13.79. Found: C, 77.35; H, 8.75; S, 14.04.

Addition of p-thiocresol to 3-methylenecyclohexene (II). To 2.20 g. (0.0234 mole) of II, 2.90 g. (0.0234 mole) of *p*-thiocresol was added in small portions. The mixture was stirred continuously with a micro thermometer. The temperature of the mixture rose to 40° during the addition. When the addition of the mercaptan was complete, the mixture was heated on a steam bath for 2 hr. The mixture was then subjected to vacuum distillation to yield 4.15 g. (81%) of 1-cyclohexenylmethyl *p*-tolyl thioether (V), b.p. 110–121° (0.07 mm.), n_D^{20} 1.5771.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.06; H, 8.25; S, 14.67. Found: C, 77.21; H, 8.41; S, 14.71.

Palladous chloride complex of 1-cyclohexenylmethyl p-tolyl thioether (V). The palladium chloride complex was prepared according to the method of Ipatieff and Friedman.[10] The thioether (300 mg., 1.37 mmoles) was stirred with an aqueous solution of 280 mg. of palladous chloride for 6 hr. The resulting precipitate was filtered and dissolved in cold acetone. The acetone solution was filtered and cold water was added until a slight turbidity appeared. The turbidity was cleared by adding a little acetone. The solution stood overnight, and reddish-brown crystals separated, which when dry weighed 350 mg. (44%), m.p. 95–97°. Two crystallizations gave an analytical sample, m.p. 98.5–100°.

Anal. Calcd. for $C_{28}H_{36}S_2PdCl_2$: C, 54.75; H, 5.86. Found: C, 54.66; H, 5.99.

When mixed with an authentic sample of the palladium chloride complex of the cyclohexenylmethyl *p*-tolyl thioether (m.p. 98–99.5°), it had m.p. 98–99.5° (see below). But its melting point was depressed by the addition of the complex of 1-cyclohexenyl-3-methyl *p*-tolyl thioether.

1-Cyclohexenylmethanol (IX). Lithium aluminum hydride, 3.23 g. (0.085 mole), was stirred in 100 ml. of dry ether in a three necked flask equipped with a mechanical stirrer, dropping funnel, and a reflux condenser. The flask was cooled in an ice salt bath and 12 g. of methyl 1-cyclohexenecarboxylate (X)[5] (0.085 mole) in 50 ml. of dry ether was added to the hydride over a period of 10 min. After the addition was complete, the reaction mixture was stirred for an additional 15 min. with cooling. The excess of hydride was decomposed by wet ether and dropwise addition of water. The ether layer was separated and the aqueous solution was extracted with three portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate, the ether was evaporated on a steam bath and the residue distilled to yield 7.0 g. (74%) of IX, b.p. 88–89° (15 mm.), n_D^{20} 1.4885 (reported[11] b.p. 98–99° (27 mm.), n_D^{25} 1.4868).

Four grams (0.0357 mole) of this alcohol and 4.06 g. (0.0357 mole) of distilled methanesulfonyl chloride were stirred in an ice salt bath. Dry pyridine, 6 g., was added to the stirred mixture over a period of 1.5 hr. The mixture was stirred for another 2 hr. The reaction mixture was poured into 60 ml. of 10% hydrochloric acid. The aqueous solution was extracted with two 100-ml. portions of ether and the ethereal solution was washed with a saturated solution of sodium bicarbonate, with water, and then dried over potassium carbonate. The ether was removed under reduced pressure. The crude product weighed 3.15 g. (46%). Its infrared spectrum showed the characteristic sulfonate bands at 7.5 μ and 8.5 μ.

1-Cyclohexenylmethyl p-tolyl thioether (V). Sodium (360 mg., 0.0156 g.-atom) was dissolved in 20 ml. of absolute ethanol and 2 g. (0.0161 mole) of *p*-thiocresol was added. Three grams (0.0157 mole) of the methanesulfonate of IX in 20 ml. of absolute ethanol was added to it. The reaction mixture was allowed to stand at room temperature for 5 days. The mixture was poured into ice cold water and the aqueous solution was extracted with three 100-ml. portions of ether. The ethereal solution was washed with 50 ml. of 3% sodium hydroxide solution, with water and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the residue distilled to give 1.77 g. (52%) of 1-cyclohexenylmethyl *p*-tolyl thioether, b.p. 118–126° (0.4 mm.). It was chromatographed through activated alumina to remove any ditolyl disulfide. The prod-

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(10) V. N. Ipatieff and B. S. Friedman, *J. Am. Chem. Soc.*, 61, 684 (1939).

(11) W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.*, 78, 2805 (1956).

uct was obtained on elution with petroleum ether, b.p. 60–70°. The chromatographed product was distilled again to prepare an analytical sample, b.p. 119–126° (0.4 mm.), n_D^{20} 1.5748.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.06; H, 8.25; S, 14.67. Found: C, 76.71; H, 8.52; S, 14.99.

The palladium chloride complex, m.p. 98–99.5°, was prepared as described above.

3-Cyclohexenylmethanol (XI). Ten grams (0.0649 mole) of 3-acetoxymethylcyclohexene,[6] was heated at reflux with an ethanolic solution of sodium hydroxide for 2 hr. Most of the ethanol was distilled under reduced pressure and the residue was diluted with 100 ml. of water. The organic layer was separated and the aqueous layer was extracted with two 50-ml. portions of ether. The combined organic solution was dried over anhydrous magnesium sulfate, the ether was evaporated and the residue distilled under vacuum to yield 4.74 g. (65%) of XI, b.p. 94–96° (15 mm.), n_D^{20} 1.4857.

3-Cyclohexenylmethyl p-tolyl thioether (VI). 3-Cyclohexenylmethanol (2.22 g., 0.0198 mole) was treated with an equivalent quantity of methanesulfonyl chloride to give 1.85 g. (49%) of the crude methanesulfonate. This was treated with sodium *p*-thiocresoxide as above to yield 1.5 g. (70%) of VI, b.p. 110–113° (0.15 mm.), n_D^{20} 1.5781.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.06; H, 8.25; S, 14.67. Found: C, 77.09; H, 8.25; S, 14.89.

Palladous chloride complex of 3-cyclohexenylmethyl p-tolyl thioether (VI). One hundred milligrams of the thioether VI was shaken with an aqueous solution of palladous chloride to give 129 mg. (45%) of the complex, m.p. 112–114°. Two crystallizations from acetone and water gave an analytical sample, m.p. 117–118°.

Anal. Calcd. for $C_{28}H_{36}S_2PdCl_2$: C, 54.75; H, 5.86. Found: C, 54.73; H, 5.80.

Acknowledgment. The authors are indebted to the National Science Foundation for support of this work.

BOULDER, COLO.

[CONTRIBUTION FROM THE BIOCHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Quaternary Heterocyclic Aldehydes and Hemiacetals

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Received April 18, 1960

1-Methyl-2- and 4-formylpyridinium and 2-formylquinolinium iodides can be obtained as crystals having characteristic and reproducible properties by separation from alcoholic solution. Elemental analyses correspond to 1:1 adducts with alcohol; the infrared spectra indicate that the products obtained are hemiacetals. 1-Methyl-2-formylpyridinium iodide accelerates the hydrolysis of isopropyl methylphosphonofluoridate in near neutral aqueous solution.

In connection with the investigation of pyridinium carboxaldoximes as potential therapeutics in the treatment of poisoning by organophosphorus anticholinesterase compounds,[1] a number of quaternary carboxaldehydes were prepared by methylation of the corresponding tertiary aldehydes (Table I). These compounds had been prepared by earlier workers by what is normally a simple and straightforward reaction and it seemed curious to find that their reported physical properties were subject to great variation. For example, one of the compounds (1-methyl-2 formylpyridinium iodide) had been reported as a liquid,[2] and as a high melting crystalline solid.[3] In most cases elemental analyses were not reported. As the substances are hygroscopic and in each case reacted in a manner consistent with the assumed structure, it seemed probable that the variations in physical properties resulted from the adsorption of moisture. We, too, initially obtained products with nonreproducible melting points; however, by careful operation under anhydrous conditions, the desired products could be obtained as crystalline solids with constant and reproducible melting points and proper elemental analyses (Table I).

It was also observed that crystalline light yellow solids having reproducible physical properties could be conveniently prepared by treatment of the 2- or 4-formylpyridinium and 2-formylquinolinium aldehydes with methyl or ethyl alcohol. Elemental analyses of these compounds, which were not the original aldehydes, correspond with 1:1 adducts of aldehyde and alcohol (Table II).

The 3-formyl-1-methylpyridinium iodide proved to be quite different from the others. It forms a relatively weakly hygroscopic, easily crystallized solid which upon treatment with methyl or ethyl alcohol gives a gum. Atmospheric drying or even repeated washing with ether results in recovery of the original aldehyde.

It is well known that carbonyl compounds form hydrates and hemiacetals when dissolved in water of alcohols.[4,5] Usually they are too unstable to be isolated. However, when the carbonyl function is attached to electron withdrawing groups, stable hydrates are frequently formed,[6] *e.g.*, chloral, glyoxal. It might be predicted that the electron withdrawing activity of the quaternary

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