1. **With 2,3-Dimethyl-1,3-butadiene.**—The product (60%) melted at 144–147°, but could not be obtained with a constant melting point; it then was stored in the solid state, and after three months melted at 162.5–164.5°. Isomerization of the product to *trans*-4,5-bis-(phenylsulfonyl)-1,2-dimethyl-1-cyclohexene had occurred (mixed m.p. 160.5°).

2. **With Cyclopentadiene.**—The product (98% yield) melted at 240–249° dec. The solid could not be recrystallized to constant melting point and, after standing for three months in the solid state, isomerized to the *trans* adduct (m.p. and mixed m.p. with the *trans* adduct 250–252.5°).

The Vilsmeyer Reaction with *trans*-1,2-Bis-(phenylmercapto)-ethylene (IIIb).—Freshly distilled N-methylformanilide (4.68 g., 34.4 mmoles) and phosphorus oxychloride (5.34 g., 34.8 mmoles) were mixed (protected from moisture), and allowed to stand for one hour. Molten *trans*-1,2-bis-(phenylmercapto)-ethylene (7.87 g., 32.1 mmoles), was then added and the mixture was allowed to stand at room temperature for 24 hours. The reaction mixture now was poured into cold water (300 ml.) and the resulting mixture was stirred for one-half hour and then extracted with chloroform. The chloroform extract was washed (water, dilute bicarbonate, water) and dried (magnesium sulfate), and the solvent was removed at reduced pressure. Attempts to crystallize the residue (9.78 g.) resulted in the isolation of small quantities of IIIb. Attempts to isolate IV as a bisulfite adduct were unsuccessful.

Reaction of the residue with acidic 2,4-dinitrophenylhydrazine[18] gave an immediate precipitate of **the 2,4-dinitrophenylhydrazone of IV.** The yield of hydrazone melting at 187–194° was 74%. The pure hydrazone melted at 200–201° (ethyl acetate).

Anal. Calcd. for $C_{21}H_{16}N_4O_4S_2$: C, 55.74; H, 3.56; N, 12.38. Found: C, 55.50; H, 3.66; N, 12.38.

Reaction of the residue with *p*-nitrophenylhydrazine[18] gave, with difficulty, the *p*-nitrophenylhydrazone of IV (m.p. 141–142°, from chloroform).

Anal. Calcd. for $C_{21}H_{17}N_3O_2S_2$: C, 61.89; H, 4.21. Found: C, 61.81; H, 4.27.

The Vilsmeyer Reaction with *cis*-1,2-Bis-(phenylmercapto)-ethylene (IIIa).—The experiment was essentially identical to that described above for the *trans* isomer. Essentially identical results were obtained (m.p. and mixed m.p. of the 2,4-dinitrophenylhydrazone of the product 199–200°).

1,1,3,3-Tetraethoxy-2-bromopropane (V).—This material (b.p. 109–112° (4 mm.), 51% yield, $n^{25}D$ 1.4399) was prepared according to the directions of Rothstein and Whitely.[10] The 1,3-diphenylimine derivative melted at 143–144° (reported[10] 145°).

Independent Synthesis of the 2,4-Dinitrophenylhydrazone of IV.—The procedure used by Rothstein and Whiteley[10] for the reaction of 1,1,3,3-tetraethoxy-2-bromopropane with ethyl mercaptan was followed.

Concentrated hydrochloric acid (1 ml.) was added to a cold (ice-bath) solution of 1,1,3,3-tetraethoxy-2-bromopropane (1 g., 3.34 mmoles), thiophenol (0.75 g., 6.68 mmoles) and acetic acid (2 ml.). The mixture was allowed to stand in an ice-bath for two hours, and was then diluted with water and extracted with ether. The ether extract was washed (water) and dried (magnesium sulfate), and the ether was removed at reduced pressure. Pyridine (3 ml.) was added to the residue, and the resulting solution was heated on a steam-bath for one-half hour. The reaction mixture was allowed to stand overnight at room temperature, and was then diluted with water and extracted with ether. Ether was removed from the dry (calcium chloride) ether extract affording 0.74 g. of residue. The 2,4-dinitrophenylhydrazone, readily prepared[18] from the residue containing the acetal, melted at 197.5–199.5 after recrystallization from ethyl acetate. A mixed melting point with the corresponding hydrazone obtained from III was 197–200°. The infrared and ultraviolet spectra of the various samples of 2,4-dinitrophenylhydrazone of IV were essentially identical.

Attempted Nitration of III.—The procedure used was identical with that previously reported for the nitration of benzo-1,4-dithiadiene.[4] The yellow oil, which separated after the nitration mixture was added to ice, solidified and was separated by filtration. The solid remelted at room temperature. Attempts to isolate a solid product by crystallization failed. The product decomposed with the elimination of oxides of nitrogen, upon attempted distillation at reduced pressure.

MINNEAPOLIS MINN.

---

[18] R. C. Fuson and R. Shriner, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, third edition, p. 229.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Ring Expansion during the Reaction of Indenylsodium and Chloroform

BY WILLIAM E. PARHAM AND HARRY E. REIFF[1]

RECEIVED OCTOBER 20, 1954

The reaction of chloroform with indenylsodium in indene gives 2-chloronaphthalene (10% yield), and a product formulated as a chloroazulene.

The Reimer–Tiemann reaction is used conventionally for the introduction of the aldehyde group into certain aromatic compounds, usually phenolic substances, capable of forming relatively stable anions. Frequently side reactions occur which lead to the formation of a variety of nonaldehydic products and/or polymeric substances Thus, in the Reimer–Tiemann reaction with phenols, dichloromethylcyclohexadienones and orthoformic esters have been formed,[2] while reaction of pyrrole and indole with chloroform and base has given rise to, respectively, 3-chloropyridine[3] and 3-chloroquinoline,[4] in addition to the expected aldehydes. A rational explanation for the production of these products lies in the postulation[5] of dichlorocarbene (II) as an intermediate, and the existence of such an intermediate in the basic hydrolysis of chloroform has strong kinetic support.[5]

It seemed reasonable to expect that the ring expansion noted for derivatives of pyrrole would obtain for certain cyclic olefins which form anions, and this has been shown to be the case. When a mixture of indene and the sodium salt of indene was treated with chloroform, a tarry reaction product resulted from which 2-chloronaphthalene

---

[1] National Science Foundation fellow 1954–1955.

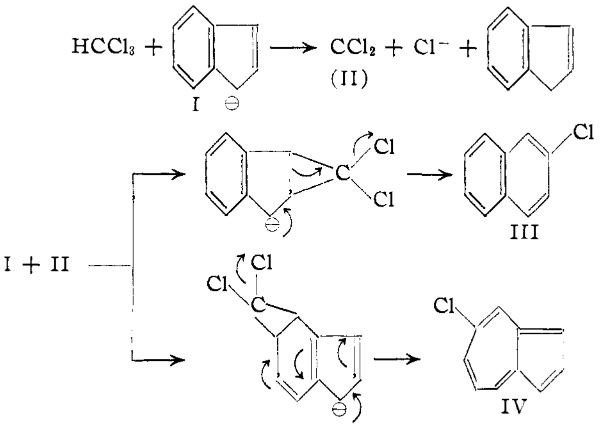
[2] K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902); J. E. Driver, THIS JOURNAL, **46**, 2090 (1924).

[3] G. L. Ciamician and M. Dennstedt, *Ber.*, **14**, 1153 (1881); **15**, 1172 (1882); O. Bocchi, *Gazz. chim. ital.*, **30**, I, 89 (1900); G. Plancher and U. Ponti, *Atti. accad. naz. Lincei*, [5] **18**, II, 473 (1909).

[4] G. Plancher and O. Carrasco, *ibid.*, [5] **13**, I, 575 (1904); G. Magnanini, *Gazz. chim. ital.*, **17**, 249 (1887).

[5] J. Hine, THIS JOURNAL, **72**, 1438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

(III) (10% yield) was isolated by steam distillation and chromatography. The 2-chloronaphthalene was identified by comparison to an authentic sample and by its conversion into the corresponding picrate.



A second product isolated from the chromatogram has not yet been obtained in a pure state; however, its chemical and physical behavior strongly suggest that it is an azulene (such as IV). Thus, the deep blue solid was sublimed easily, and could be extracted from petroleum ether solutions with phosphoric acid. The ultraviolet and visible spectra of the impure azulene showed absorption maxima at or near those wave lengths at which azulenes absorb,[6,7] notably the 310–370 mμ and the 600–750 mμ region; however, the instability of this product[7] has precluded further purification.

Doering and Hoffman have shown recently that dichlorocarbene readily adds to olefins,[8] and the formation of an azulene in the reaction with indene could be explained by assuming attack of the dichlorocarbene on the benzene ring as shown in the equation above.

Experimental

Indenylsodium was prepared by heating 11.5 g. (0.5 g.-atom) of sodium in excess indene (250 g. purified through the sodium salt) at 130–150° under nitrogen.

To a cooled, well-agitated mixture of indenylsodium and indene was added 66 g. (0.55 mole) of dried, redistilled chloroform, over a period of 15 minutes. The mixture was stirred for one hour at room temperature, and the resulting dark red solution was quenched on ice and the quench mixture steam-distilled. The distillate was extracted with ether, the blue ethereal solution dried, and ether removed by distillation. Approximately 150 g. of indene was distilled from the residue at reduced pressure; the new residue was then chromatographed on 200 g. of alumina using petroleum ether (boiling range 60–68°) as solvent and developer. A blue band traveled with the solvent front and was eluted. The eluates were concentrated, and after combination additional indene was removed from the concentrate by fractionation at 0.4 mm. and a pot temperature not exceeding 60°. The dark blue solid residue (5 g.) was chromatographed on 280 g. of alumina using petroleum ether as solvent and developer. The initial eluates were essentially colorless, and upon concentration solidified to give 4.1 g. (10%) of 2-chloronaphthalene, m.p. 59.0–59.5°. An authentic sample of 2-chloronaphthalene, prepared from β-naphthylamine,[9] melted at 59.5–60.0° (mixed melting point 59.0–59.5°). The infrared spectra of the two samples were identical.

Anal. Calcd. for $C_{10}H_7Cl$: C, 73.85; H, 4.34. Found: C, 73.65; H, 4.77.

The 2-chloronaphthalene was further characterized by conversion[10] into its picrate (m.p. and mixed m.p. 84–85°).

The blue eluate from the chromatogram was concentrated to give 0.5 g. of a dark blue solid. This material was dissolved in 10 ml. of petroleum ether and extracted with 10 ml. of chilled 85% phosphoric acid. The yellow-brown phosphoric acid layer was washed with petroleum ether and then quenched in an ice-water–petroleum ether mixture, whereupon the blue color was regenerated. Concentration of the petroleum ether layer afforded 0.1 g. of a dark blue solid. The material decomposed slowly at room temperature into a dark, petroleum ether-insoluble, product. Losses accompanying sublimation of the material amounted to greater than 50%. The ultraviolet and visible spectra of a solution of the blue sublimate in cyclohexane showed peaks at 227, 279, 301, 321, 327, 331, 342, 346, 358, 605, 628, 665, 695 and 735 mμ. The visible spectrum was essentially identical to that reported[7] for 1-chloroazulene, but displaced by about 5 mμ toward the ultraviolet. The extinction coefficients in the visible and ultraviolet regions were approximately 40% of those reported for 1-chloroazulene.

MINNEAPOLIS, MINNESOTA

---

(6) Pl. A. Plattner and A. St. Pfau, *Helv. Chim. Acta*, **20**, 224 (1937); W. Reppe, O. Schlichting and H. Meister, *Ann.*, **560**, 93 (1948).

(7) A. G. Anderson, J. J. Tazuma and J. A. Nelson, THIS JOURNAL, **75**, 4980 (1953), report that 1-chloroazulene is too unstable to permit analysis.

(8) W. von E. Doering and A. K. Hoffman, 126th Meeting of the American Chemical Society, New York, September 14, 1954, Abstracts of Papers, p. 43-O.

(9) K. Scheid, *Ber.*, **34**, 1813 (1901).

(10) N. Jefremow, *J. Russ. Phys. Chem. Soc.*, **50**, 381 (1918), reports the melting point of this derivative as 81.5°.