Reaction of ethyl bromide and phenyl Grignard reagent with active cobalt metal produced via sodium-naphthalene complex. A solution of sodium-naphthalene complex was prepared by treating 2.40 g. (0.104 mole) of finely dispersed sodium with 14.0 g. (0.109 mole) naphthalene in 150 ml. of tetrahydrofuran (dried by distillation from lithium aluminum hydride). To this solution was added 6.00 g. (0.0465 mole) of cobaltous chloride (dehydrated by the thionyl chloride method[7]) and the solution was stirred for 2 hr. after the initial vigorous reaction, during which brown-black solids were precipitated. The walls of the flask were rinsed with 40–50 ml. of fresh tetrahydrofuran to remove adhering cobaltous chloride and assure complete reduction to the metal. The resultant mixture was then treated with 7.85 g. (0.072 mole) of ethyl bromide and the formation of gaseous products was observed. A total of 27 cc. of gas (at S.T.P.) was evolved, probably from interaction of the excess sodium-naphthalene complex with ethyl bromide. To the same solution then was added 50 ml. of a tetrahydrofuran solution of phenyl Grignard reagent prepared from 1.30 g. (0.053 g.-atom) of magnesium metal and 7.85 g. (0.050 mole) of bromobenzene. An immediate evolution of gas occurred and the reaction mixture became warm. A total of 261 cc. of gas was evolved, 23% of the theoretical amount of available ethyl groups. This is somewhat lower than the 48% evolution observed by Smith,[4] but the difference can be attributed to the use of a larger volume of solvent in this case. Analysis of the gas indicated that it was primarily ethylene and ethane in a mole ratio of 1.3 to 1.[8] The reaction mixture was heated to the reflux temperature to evolve an additional 592 cc. of gas containing ethylene and ethane in a mole ratio of 1.3 to 1. No attempt was made to calculate total yield of gaseous products as no correction was made for gas displaced by vaporization of the tetrahydrofuran at reflux. The ethane to ethylene ratio is in good agreement with that reported by Kharasch, Lewis, and Reynolds[5] for the same reaction in the absence of sodium-naphthalene complex.

Stepwise reaction of phenyl Grignard reagent with cobaltous chloride and ethyl bromide followed by addition of more phenyl Grignard reagent. To 50 ml. of phenyl Grignard reagent (0.044 mole, prepared from bromobenzene and magnesium turnings in tetrahydrofuran) was added 2.82 g. (0.022 mole) of cobaltous chloride in a nitrogen box. Considerable heat was evolved and a dark brown precipitate was produced immediately. The reaction mixture was heated at reflux for 1 hr. To the cooled reaction mixture was added 10.22 g. (0.094 mole) of ethyl bromide. A total of 18 cc. (at S.T.P.) of gas was evolved upon addition of the ethyl bromide. After 30 min., a second 50-ml. aliquot of the Grignard reagent (0.044 mole) was added. Immediate evolution of gas occurred. A total of 615 cc. of gas was evolved at room temperature and an additional 260 cc. (corrected for vapor displacement) was collected when the solution was heated to reflux. After standing overnight, the solution was treated with another 48 ml. of Grignard reagent (0.042 mole). Again an immediate gas evolution occurred. A total of 500 cc. of gas was collected at room temperature and an additional 305 cc. of gas was evolved upon heating to reflux. The 875 cc. of gas (total) evolved upon the first addition is equivalent to 90% of theory. Mass spectographic analyses of the evolved gases at periodic intervals showed the mole ratios of ethylene to ethane to be between 1.2 and 1.4 to 1.

The reaction mixture was diluted with petroleum ether (b.p. 30–60°), extracted with dilute aqueous acid, and filtered. From the cold, concentrated filtrate was isolated 4.5 g. of biphenyl, (m.p. 69–69.5° uncorrected) equivalent to

45% of the phenyl groups charged originally as phenyl Grignard reagent. Mass spectographic analysis of the residual liquor showed ethylbenzene to be present, but no quantitative analyses were made.

The experiment was repeated using 2.60 g. (0.020 mole) of cobaltous chloride, 0.041 mole of phenyl Grignard reagent, and a stoichiometric quantity of ethyl bromide (0.041 mole). No gas was evolved. A second addition of 0.041 mole of phenyl Grignard reagent caused the evolution of 658 cc. of gas (at S.T.P.), equivalent to 73% of the ethyl values charged as ethyl bromide. Mass spectographic analysis showed the gases to contain primarily ethylene and ethane (mole ratio 1.3 to 1). Repeated extraction of the filtered reaction mixture with water produced a small volume of a dark water-immiscible liquid. Gas chromatographic analysis of this liquid gave two strong peaks with elution times identical to those obtained with standards of ethylbenzene and biphenyl. No quantitative determinations were made.

Addition of Hydrogen Bromide to the Nitrostyrenes[1]

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The addition of hydrogen bromide to styrene under ionic conditions gives α-phenethyl bromide, $C_6H_5CHBrCH_3$, to the exclusion of the β-isomer.[2] This result, similar to the ionic addition of hydrogen bromide to propylene to give isopropyl bromide,[3] has been explained somewhat vaguely in terms of electron-donation by the alkyl group attached to the ethylenic system[4]: $R—C=CH_2$. In the case of styrene, such an explanation would appear rather unattractive, however, since the inductive effect of the phenyl group is quite clearly electron withdrawing rather than electron donating. A more plausible explanation of the Markovnikov sense of addition of hydrogen bromide to olefins of the type $R—CH=CH_2$ is in terms of a product-determining intermediate or transition state of type $R—\overset{+}{C}H—CH_3$ which is favored over the alternate $R—CH_2—$

(1) Presented in part before the Division of Organic Chemistry at the Buffalo, N. Y., Meeting of the American Chemical Society, March 1952.

(2) C. Walling, M. S. Kharasch, and F. R. Mayo, *J. Am. Chem. Soc.*, 61, 2693 (1939).

(3) F. R. Mayo and M. G. Savoy, *J. Am. Chem. Soc.*, 69, 1348 (1947). The reaction is not as clean-cut as is implied in some textbooks.

(4) *e.g.* R. Q. Brewster and W. E. McEwen, *Organic Chemistry*, 3rd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1961, p. 73 for the case of the addition of hydrogen iodide to propylene.

(7) A. R. Pray, *Inorganic Syntheses*, **Vol. V**, McGraw-Hill Book Company, Inc., New York, N. Y., 1957, p. 154.

(8) The evolved gases always contained small amounts of butane and tetrahydrofuran. Higher hydrocarbons were not detected. In all experiments the molar concentrations of butane and tetrahydrofuran were each less than 1% of the total.

CH_2^+ through resonance or hyperconjugation involving the group R.[5]

A clear-cut distinction between the two explanations can be made by observing the sense of addition of hydrogen bromide to the nitrostyrenes. For whereas benzoic acid, pK_a 4.17, for reasons probably unrelated to the inductive effect of phenyl, is a weaker acid than formic (pK_a 3.77), the nitrobenzoic acids are all stronger than formic (*ortho*, pK_a 2.21, *meta*, pK_a 3.46, *para*, pK_a 3.40) and the nitrophenyl group is therefore unequivocally an electron-withdrawing and not an electron-donating group. Thus, if the inductive effect of the R-group in R—CH=CH₂ (relative to hydrogen) dictates the sense of addition, the nitrostyrenes should add hydrogen bromide to give R—CH₂—CH₂Br. But if resonance or hyperconjugative stabilization of a positively charged intermediate or transition state is paramount, the product should be R—CHBr—CH₃ because of the presence of the canonic forms shown below.

(two forms)

unfavorable
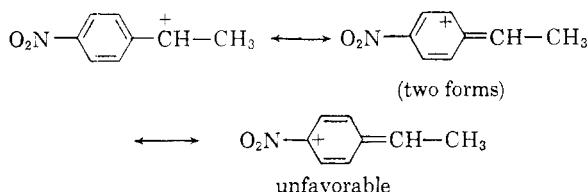
Two other *a priori* observations may be made. First, since the nitro group is generally inhospitable to the development of positive charge in the intermediate or transition state shown above, addition of hydrogen bromide to the nitrostyrenes by an electrophilic mechanism should be slower than the corresponding addition to styrene, and the retardation should be most marked in the *ortho* and *para* isomers (where the positive charge in one of the canonic forms is lodged right next to the electron-withdrawing nitro group). Secondly, if the product of the addition of hydrogen bromide to *o*- and *p*-nitrostyrene were the *β*-bromide, (O₂NC₆H₄CH₂—CH₂Br), the possibility of a nucleophilic addition—similar to the addition of hydrogen bromide to methyl acrylate, CH₂=CHCO₂CH₃, which gives the *β*-bromopropionate, CH₂BrCH₂CO₂CH₃[6]—would have to be envisaged, since cases of nucleophilic addition to these nitrostyrenes have been reported in the literature.[7]

In actual fact, the addition of hydrogen bromide to both *m*- and *p*-nitrostyrene in benzene solution gave nearly evclusevely the corresponding *α*-bromide, O₂NC₆H₄CHBrCH₃. The *para* isomer

was a crystalline solid melting at 35.0–35.5°, different from the known *β*-bromide and identical with the product of photochemical bromination of *p*-nitroethylbenzene. *α*-(*m*-Nitrophenyl)-ethyl bromide was also crystalline, melting at 42–43°; its structure was proved by hydrolysis to the known[8] alcohol and confirmed by spectroscopy. Control experiments in the *para* series indicated that if as much as 5% of the *β*-bromide had been formed in the addition, it could have been readily detected by infrared and NMR spectroscopy and that the *β*-bromide is stable to treatment with aluminum bromide under the conditions of the reaction (see below) and toward vacuum distillation, used in the isolation of the reaction product.

Addition of hydrogen bromide gas to styrene proceeds readily at room temperature.[2] In contrast, the addition to *m*-nitrostyrene in benzene solution required the presence of aluminum bromide as a catalyst. Alternatively, the addition could be carried out in the absence of a catalyst at 100° in acetic acid solution in a sealed tube. Addition of hydrogen bromide to *p*-nitrostyrene proceeded only in the presence of the aluminum bromide catalyst and addition to *o*-nitrostyrene failed under all conditions that were tried.

The conclusion may be reached that the addition of hydrogen bromide to the nitrostyrenes is an electrophilic addition which is slowed down by the nitro substituents in the ring (more so by a *para* than by a *meta* substituent, whereas an *ortho* substituent suppresses the addition altogether). The direction of addition is as expected on the basis that an *α*-phenethyl cation intermediate (or similar transition state) is stabilized by resonance whereas the corresponding *β*-phenethyl cation is not.

EXPERIMENTAL

Nitrostyrenes. *m*-Nitrostyrene was prepared by decarboxylation of *m*-nitrocinnamic acid,[9] b.p. 56–59°/0.1 mm. (lit.[9] b.p. 96°/3.5 mm.), n_D^{20} 1.5838 (lit.[9] n_D^{20} 1.5830). *p*- and *o*-Nitrostyrene were prepared by dehydrobromination of the corresponding *β*-(nitrophenyl)ethyl bromides,[10] or more conveniently, by decarboxylation of the appropriate nitrocinnamic acid, as described[9] for the *meta* isomer. *p*-Nitrostyrene melted at 19.5–20.5° (lit.[10] m.p. 21.4°). *o*-Nitrostyrene boiled at 70–74°/0.4–0.5 mm., n_D^{25} 1.5850 and melted at 9–10° (lit.[11] m.p. 13–14°).

α-(*m*-Nitrophenyl)ethyl bromide. Addition of hydrogen bromide to *m*-nitrostyrene. (a) A solution of 7.5 g. (0.093 mole) of hydrogen bromide gas and 4 g. (0.027 mole) of *m*-nitrostyrene in 30 g. of glacial acetic acid was heated at 100° in a sealed tube for 2.5 hr. The acetic acid was removed by vacuum distillation and the residue distilled, b.p. 100–120°/1.5 mm., m.p. 40–41°, yield 5.2 g. (85%). Recrystallization from petroleum ether (b.p. 30–60°) raised the m.p. to 41–42°.

(b) To a solution of 1 g. of aluminum bromide in 50 ml. of

(5) *e.g.* R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn & Bacon, Inc., Boston, Mass., 1959, pp. 141 and 277.

(6) R. Mozingo and L. A. Patterson, *Org. Syntheses*, Coll. Vol. III, 576 (1955) after C. Moureu, M. Murat, and L. Tampier, *Ann. chim.*, [9] 15, 221 (1921).

(7) W. J. Dale and C. W. Strobel, *J. Am. Chem. Soc.*, 76, 6172 (1954).

(8) M. Lund, *Ber.*, 70, 1520 (1937).

(9) R. H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, 70, 2295 (1948).

(10) R. W. Strassburg, R. A. Gregg, and C. Walling, *J. Am. Chem. Soc.*, 69, 2141 (1947).

(11) B. Lüning, *Acta Chem. Scand.*, 11, 959 (1957).

dry benzene was added dropwise with stirring 5 g. (0.033 mole) of *m*-nitrostyrene while dry hydrogen bromide gas was bubbled through the solution. The solution turned dark red. Addition took 0.5 hr. and the passage of hydrogen bromide was continued for 2.5 hr. more. The reaction mixture was then poured into ice water and the benzene layer was separated, washed three times with dilute sodium bicarbonate solution and three times with water, dried over calcium chloride, and concentrated. The residue was distilled at 0.6 mm. and collected in two fractions, b.p. 110–115° and 115–130°. Both fractions solidified on standing in the refrigerator, m.p. 40.5–41.5° and 38–41°, combined yield 5.3 g. (70%). Recrystallization raised the m.p. to 42–43°.

Anal. Calcd for $C_8H_8BrNO_2$: C, 41.76; H, 3.50. Found: C, 41.84; H, 3.47.

α-(m-Nitrophenyl)ethyl alcohol. The above bromide (1.5 g.) was boiled for 24 hr. with a solution of 4.0 g. lead nitrate in 60 ml. of water. Upon cooling the organic material solidified. It was extracted into ether and the ether layer dried over calcium chloride and concentrated. The residue crystallized when chilled in Dry Ice–acetone and, upon recrystallization, melted at 59–60°. The mixture melting point with an authentic sample of α-(*m*-nitrophenyl)ethyl alcohol, m.p. 60–61° (lit.[8] m.p. 62.5), prepared by reduction of *m*-nitroacetophenone with sodium borohydride in methanol, was 60–61.5°.

α-(p-Nitrophenyl)ethyl bromide. (a) *By addition of hydrogen bromide to p-nitrostyrene.* Five grams of *p*-nitrostyrene was subjected to procedure (b) described above for *m*-nitrostyrene. The product was distilled at 0.6 mm. and collected in four fractions: (1) b.p. below 100° (1.0 g.); (2) b.p. 100–126° (1.0 g.); (3) b.p. 126–135° (2.5 g.); (4) 135–138° (1.0 g.). Fractions 2, 3, and 4 solidified upon cooling in Dry Ice–methanol and upon recrystallization from petroleum ether melted at 33–34°. Further recrystallization raised the melting point to 35.0–35.5°.

The infrared spectrum of fraction 1 above indicated it to be mainly recovered *p*-nitrostyrene (characteristic bands at 922 and 987 cm.⁻¹). Fractions 2–4 were mainly α-(*p*-nitrophenyl)-ethyl bromide containing decreasing amounts of *p*-nitrostyrene as an impurity; thus the yield of the bromide was *ca.* 4.5 g. or 73% based on 4 g. of starting material consumed. A careful inspection was made for the presence of β-(*p*-nitrophenyl)ethyl bromide in fractions 3 and 4, since a comparison sample of this bromide, m.p. 67.0–69.5° (lit.[10] m.p. 69–70.5°) was available from the preparation of *p*-nitrostyrene. The β-bromide has a characteristic infrared band at 1263 cm.⁻¹ which is absent in the α-isomer. Comparison of the infrared spectra of fractions 3 and 4 with spectra of synthetic mixtures of the isomeric bromides indicated that the addition product of *p*-nitrostyrene and hydrogen bromide contained less than 5% of the β-bromide. This conclusion was confirmed by the NMR spectra of fractions 3 and 4 which were identical with that of the pure α-bromide and did not show the complex multiplet due to the methylene protons which appears in the spectrum of the pure β-bromide. A mixture of 95% α- and 5% β-bromide clearly showed this multiplet in between the methyl doublet and the methine quartet of the α-bromide.

(b) *By photobromination of p-nitroethylbenzene.*[12] Eleven grams of *p*-nitroethylbenzene was brominated in carbon tetrachloride using a 500-watt tungsten projector lamp as light source.[12] The product, 12.9 g. (77%) boiled at 107–114°/0.3–0.4 mm. (lit.[12] b.p. 152–153°/5 mm.) and solidified on cooling (not previously reported.[12]) Recrystallization from petroleum ether gave material melting at 35.0–35.5°; mixture melting point with addition product of *p*-nitrostyrene and hydrogen bromide, 35.0–35.5°.

(12) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, 71, 3482 (1949) following the procedure of W. M. Cumming, I. V. Hopper, and T. S. Wheeler, *Systematic Organic Chemistry*, 4th ed., Constable and Co., Ltd., London, England, 1950, p. 358.

Controls. Attempted addition of hydrogen bromide to o-nitrostyrene. The attempted addition of hydrogen bromide to *p*-nitrostyrene in pentane, in high-boiling petroleum ether at 90–100° and in acetic acid in a sealed tube failed, *p*-nitrostyrene being recovered. Treatment of β-(*p*-nitrophenyl)-ethyl bromide with aluminum bromide in benzene under the conditions of the addition reaction led to recovery of starting material in over 73% yield. Distillation of a mixture of 2.0 g. of α-bromide and 0.4 g. of β-bromide at 0.6 mm. returned 0.75 g. material of b.p. 120–126° and 0.95 g. of b.p. 126–128°. Both fractions were shown, by NMR spectroscopy, to contain about 15–20% β-bromide.

Attempted addition of hydrogen bromide to *o*-nitrostyrene in the presence of aluminum bromide in varying proportions gave only unchanged *o*-nitrostyrene or intractable high-boiling materials. A dark-colored complex appeared to form between the olefin and the catalyst in benzene solution.

Ylides from *o*-Xylylene Dipyridinium Salts

WILLIAM E. ROSEN

In the course of our attempts to prepare 4,5,6,7-tetrachloroisoindoline derivatives,[1,2] we have studied the reaction of tetrachloro-*o*-xylylene dipyridinium salts (IIc and IId) with methylamine. The preparation of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) from Ic, as of *o*-xylylene dipyridinium dibromide (IIa) itself from Ia, was straightforward. In contrast, the preparation of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium di-*p*-toluenesulfonate (IId) from Id (with *p*-toluenesulfonyl chloride in pyridine), unlike the preparation of *o*-xylylene dipyridinium di-*p*-toluenesulfonate (IIb) from Ib, was complex. The yield of IId was low, even in the presence of excess *p*-toluenesulfonyl chloride, and the monopyridinium salts IIIa and IIIb were isolated as by-products.[3]

Treatment of the dibromide IIc or the di-*p*-toluenesulfonate IId with aqueous methylamine gave no isoindoline. Instead, methylamine abstracted a proton from a benzyl carbon atom, and generated the corresponding ylide (IVb or IVc, respectively) in 85% yield. Aqueous ammonia or aqueous potassium hydroxide generated IVb from

(1) W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, 79, 3167 (1957).

(2) W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, 80, 935 (1958).

(3) Treatment of the pyridine-insoluble monopyridinium tosylate IIIa with excess *p*-toluenesulfonyl chloride in pyridine for seven days gave a 94% yield of dipyridinium dichloride (IIe).