reductions reported below was filtered from the water and washed with two 20-ml. portions of absolute ethanol and two 20-ml. portions of acetic anhydride. Catalyst so treated lost activity rapidly if allowed to stand under acetic anhydride.

Reduction of tridecanenitrile. A 2–3 g. portion of Raney nickel treated as described above and 12.0 g. of anhydrous sodium acetate were added to a solution of 19.5 g. (0.10 mole) of tridecanenitrile in 120 ml. of acetic anhydride. The resulting mixture was heated to 50° and shaken under hydrogen at an initial pressure of 50 p.s.i. After about 1 hr. hydrogen uptake was complete, and the catalyst was filtered from the hot solution. When the filtrate was cooled in ice, a white solid precipitated. After recovery and drying, this amounted to 24.1 g. (100%) of *N*-acetyltridecylamine, m.p. 57–58°.

Anal. Calcd. for $C_{15}H_{31}ON$; C, 74.62; H, 12.94; N, 5.80. Found: C, 74.62; H, 13.04; N, 5.44.

Reduction of benzonitrile. A mixture of 2–3 g. of treated Raney nickel, 10.3 g. (0.10 mole) of benzonitrile, and 120 ml. of acetic anhydride was shaken at 50° under an initial hydrogen pressure of 50 ps.i. When the reaction was complete (1 hr.), the mixture was filtered hot and the filtrate was treated with 40 ml. of water. Then 180 ml. of concd. hydrochloric acid was added, and the mixture was heated under reflux for 16 hr. The resulting solution was cooled to 25°, made strongly basic with 5*N* sodium hydroxide solution, and extracted with two 100-ml. portions of ether. The ether solution was dried over anhydrous magnesium sulfate, filtered, and treated with gaseous hydrogen chloride until no further precipitate formed. After recovery and drying, there was obtained 13.0 g. (91%) of benzylamine hydrochloride, m.p. 248–249° (lit.,[5] m.p. 248°).

Reduction of acrylonitrile. A mixture of 2–3 g. of treated Raney nickel, 5.3 g. (0.10 mole) of acrylonitrile, 12.0 g. of anhydrous sodium acetate, and 120 ml. of acetic anhydride was shaken at 25° under hydrogen at an initial pressure of 50 p.s.i. Hydrogen uptake was complete after 16 hr., and the catalyst was removed by filtration. The filtrate was treated with 40 ml. of water and the mixture was allowed to stand with occasional stirring for 3 hr. Then 180 ml. of concd. hydrochloric acid was added, and the mixture was heated under reflux for 16 hr. After cooling to 25° the solution was made strongly basic with 5*N* sodium hydroxide solution and was stirred for 2 hr. with 16.8 g. (0.12 mole) of benzoyl chloride. The solid which separated was recovered by filtration and dried. There was thus obtained 15.0 g. (92%) of *N*-propylbenzamide, m.p. 84–85° (lit.,[6] m.p. 84–85°).

Reduction of adiponitrile. A mixture of 10.8 g. (0.10 mole) of adiponitrile, 2–3 g. of treated Raney nickel, 4.4 g. of solid sodium hydroxide, and 120 ml. of acetic anhydride was shaken with hydrogen under 50 p.s.i. pressure, and the temperature was raised cautiously to 50°. At this point a vigorously exothermic reaction set in, and, although the heater was cut off, the temperature rose rapidly to 75° and then dropped slowly. Hydrogen uptake was complete in 15 min. The reaction mixture was filtered hot and the filtrate was cooled in ice to precipitate the product. After recovery and drying there was obtained 16.0 g. (80%) of *N,N'*-diacetylhexamethylenediamine, m.p. 125–126°. (lit.,[7] m.p. 125–126°).

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[5] I. Heibron and H. M. Bunbury, *Dictionary of Organic Compounds,* Vol. I, Oxford Univ. Press, N. Y., 1953, p. 270.

[6] I. Heibron and H. M. Bunbury, *Dictionary of Organic Compounds,* Vol. IV, Oxford Univ. Press, N. Y., 1953, p. 243.

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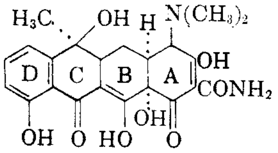
Selective Reactions of the Butadiene-Methoxybenzoquinone Adduct

GEORGE I. BIRNBAUM[1]

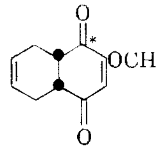
Received February 29, 1960

A recent publication by Barltrop and Burstall[2] prompts us to report our work with potential intermediates in a synthesis of tetracycline (I). We prepared 2-methoxy-4a,5,8,8a-tetrahydronaphthoquinone (II) in 85% yield. Further utilization of molecules of this type to elaborate rings A and B of tetracycline requires the introduction of the *N,N*-dimethylamino group in the place of the starred carbonyl. Selective reactions of this carbonyl were expected to be feasible since the other carbonyl group is deactivated by being conjugated with a free pair of electrons on the oxygen of the methoxy group. We were indeed successful in certain selective reactions. Compound II can be reduced selectively by sodium borohydride to give in 44% yield the keto alcohol IIIa. Its *p*-toluenesulfonate (IIIb) was prepared, but an attempt to prepare compound IVa by a displacement of the *p*-toluenesulfonate group was not successful as no reaction took place upon refluxing IIIb with diethylamine.

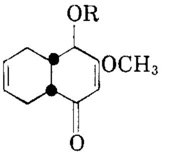
The monoxime of II, compound V, was also prepared in good yield. Catalytic hydrogenation of V with palladium-charcoal did not, however, yield the desired amine IVb.



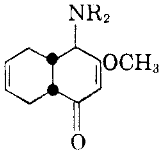
I



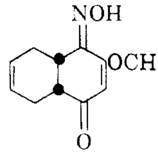
II



IIIa, R = H
b, R = p-$CH_3C_6H_4SO_2$



IVa, R = C_2H_5
b, R = H



V

EXPERIMENTAL[3]

2-Methoxy-4a,5,8,8a-tetrahydronaphthoquinone (II). Methoxybenzoquinone[4] (8.50 g.) and 15 ml. of dry benzene were placed in a heavy-walled glass tube cooled by Dry Ice. To

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[2] J. A. Barltrop and M. L. Burstall, *J. Chem. Soc.,* 2183 (1959).

[3] Melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[4] Prepared by the procedure of Ioffe and Sukhina, *J. Gen. Chem.,* **23,** 295 (1953), [*Chem. Abstr.* **48,** 2640d].

this suspension there was added 20 ml. of condensed butadiene and several crystals of hydroquinone to inhibit polymerization. The sealed tube was kept at 115° for 40 hr. After several crystallizations from ether 10.0 g. of white crystals, m.p. 126–127.5°, was obtained (85% yield). $\lambda_{max}^{CHCl_3}$ = 5.88 μ (unconjugated ketone), 6.04 μ (conjugated ketone), 6.24 μ (enol ether).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.30. Found: C, 68.36; H, 6.12.

2-Methoxy-4-oxo-1,4,4a,5,8,8a-hexahydro-1-naphthol (IIIa). Sodium borohydride (0.20 g.) was dissolved in 70 ml. of ethanol and a solution of 0.96 g. of II in 10 ml. of ethanol was added dropwise. The flask was allowed to stand for 3 hr., then water was added. The solution was saturated with sodium chloride and extracted with ether. Upon recrystallization from cyclohexane 0.20 g. (44% yield) of white, fibrous crystals, m.p. 134–135°, was obtained. $\lambda_{max}^{CHCl_3}$ = 6.05 μ, 6.20 μ.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.03; H, 7.27. Found: C, 68.06; H, 7.18.

The *p-toluenesulfonate* (IIIb) crystallized from methanol as white crystals, m.p. 93°.

Anal. Calcd. for $C_{18}H_{19}O_5S$: C, 62.23; H, 5.51. Found: C, 62.35; H, 5.60.

2-Methoxy-4a,5,8,8a-tetrahydronaphthoquinone-1-oxime (V). To a solution of 0.35 g. (0.005 mole) of hydroxylamine hydrochloride in 5 ml. of pyridine and 5 ml. of absolute ethanol there was added 0.96 g. (0.005 mole) of II. The solution was refluxed for 1 hr. After it had cooled the solvents were blown off by a stream of air. The residue was triturated with 5 ml. of cold water and filtered. The oxime was recrystallized from methanol to give white crystals which begin to decompose at 200°. The yield amounted to 0.65 g. (68%). $\lambda_{max}^{CHCl_3}$ = 6.08 μ, 6.28 μ.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 64.03; H, 6.28; N, 6.89.

Acknowledgment. The author wishes to express his gratitude to Professor Gilbert Stork for his interest in this work.

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Synthesis of Some Haloolefins. Addition of Dibromodifluoromethane and Bromotrichloromethane to Vinylidene Fluoride

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Received February 22, 1960

The addition reactions of dibromodifluoromethane to vinylidene fluoride, initiated by benzoyl peroxide, proceeded as described in the literature[1,2] and comparable yields were obtained. In addition to the simple one-to-one adduct (I) an approximately equivalent amount of the two-to-one adduct (II) was isolated. It is of interest to note that this

$$CH_2{=}CF_2 + CF_2Br_2 \xrightarrow{(C_6H_5COO)_2}$$
$$\text{I}$$
$$CF_2BrCH_2CF_2Br \xrightarrow[CF_2Br_2]{(C_6H_5COO)_2}$$
$$CF_2BrCH_2CF_2CH_2CF_2Br \xrightarrow[\substack{\text{and}\\ -2HBr}]{-HBr}$$
$$\text{II}$$
$$\underset{\text{III}}{CF_2{=}CHCF_2CH_2CF_2Br} + \underset{\text{IV}}{CF_2{=}CHCF_2CH{=}CF_2}$$

reaction occurred as it did, in spite of the fact that over 400% molar excess of the halomethane was used. The 1,5-dibromo-1,1,3,3,5,5-hexafluoropentane (II) was dehydrohalogenated to the unconjugated pentadiene (IV) 1,1,3,3,5,5-hexafluoropentadiene-1,4 and some pentene (III), the 5-bromo-1,1,3,3,5,5-hexafluoropentene-1. These results substantiate the work of Hauptschein, *et al.*,[3] on telomers of fluorinated olefins.

As a corollary of this work the polymerizability of the diene was studied.[4] While the diene did not homopolymerize, it formed copolymers with butadiene, styrene, and vinyl acetate. The diene is substituted with fluorine on the carbon atom *alpha* to the sites of unsaturation ($CF_2{=}CHCF_2CH{=}CF_2$) and thus not possessed of allylic hydrogen atoms. Therefore, it should not show the retarding influence of free-radical polymerization commonly associated with allylic compounds. This advantage was probably more than offset by the fact that free-radical attack would be predicted to occur at carbon atom 2 and would doubtlessly be sterically inhibited.

Another reaction investigated was that of the peroxide-initiated addition of bromotrichloromethane to vinylidene fluoride. Although this reaction has not been reported previously, it would be expected to occur quite readily. The complication of the formation of appreciable amounts of the two-to-one adduct should be lessened because of the high chain transfer tendency of bromotrichloromethane. This proved to be the case; yields of the adduct (V), 1,1,1-trichloro-3-bromo-3,3-difluoropropane, in the neighborhood of 60% were obtained consistently.

In attempting to dehydrohalogenate the halopropane, with aqueous and ethanolic base, no products could be isolated. In one reaction with aqueous sodium hydroxide, the reaction mixture sparked, possibly due to the formation of an unstable halogen substituted acetylene derivative. Triethylamine proved to be a useful reagent for effecting the dehydrohalogenation, although even here the high reactivity of the initial reaction prod-

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