dried over either anhydrous magnesium sulfate or anhydrous sodium sulfate. The nuclear magnetic resonance (nmr) spectra ($CDCl_3$, TMS internal standard) were recorded by Miss K. Reimer using a Varian A-60 spectrometer. Gas–liquid chromatography was performed with a Varian 1200 instrument (flame ionization detector) using nitrogen as carrier gas. Elemental microanalytical data was provided by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach uber Engelskirchen, West Germany. Mass spectral data was obtained by Mr. R. Scott, employing an Atlas CH-4B mass spectrometer equipped with a molecular beam inlet system.

Tetraethyl 1-Pentene-1,1,3,3-tetracarboxylate (Ethyl α,γ-Dicarbethoxy-α-ethylglutaconate).—The following method is a modification of those reported by Ingold and Perren,[6b] for the preparation of the sodium salt of tetraethyl 1-propene-1,1,3,3-tetracarboxylate, and Thole and Thorpe,[4] for the ethylation reaction.

Sodium (46 g, 2 mol) was dissolved in ethanol (absolute, 750 ml). Diethyl malonate (160.2 g, 1 mol) was added over 30 min with heating and stirring and the mixture was heated at reflux for a further 15 min. Heating was stopped and, as soon as reflux had subsided, chloroform (60.5 g, 0.51 mol) was added at a rate sufficient to maintain vigorous reflux (over 15 min). Heating was resumed and the mixture was heated at reflux for 3 hr. The apparatus was arranged for distillation and 110 ml of the solvent was distilled from the reaction vessel.[10] The apparatus was returned to the reflux position, ethyl iodide (85.8 g, 0.55 mol) was added over 10 min, and the mixture was refluxed for a further 36 hr. After cooling the reaction mixture was poured into water (750 ml) and extracted with chloroform (10 × 200 ml). The chloroform layer was washed with potassium hydroxide solution (10%, 5 × 200 ml) and water (5 × 200 ml) and dried, and the solvent was removed under reduced pressure to give an orange oil (203.2 g). Fractionation (Vigreux column) gave tetraethyl 1-pentene-1,1,3,3-tetracarboxylate (46–63%), bp 153–157° (1.5 mm) [reported[4] bp 213° (20 mm)]. The nmr spectrum showed δ 0.88 (3 H, triplet, J = 7.6 Hz, protons on C-5 coupled to C-4 methylene protons), 1.28 and 1.325 (12 H, two triplets, J = 7.1 Hz, methyl protons), 2.22 (2 H, quartet, J = 7.6 Hz, protons on C-4 coupled to C-5 methyl protons), 4.0–4.5 (8 H, complex methylene multiplet), 7.61 ppm (1 H, singlet, vinylic proton on C_2).

Triethyl 3-Ethyl-1(2)-pentene-1,1,3-tricarboxylate (Ethyl α-Carbethoxy-γ-ethylglutaconate) (3a).—Sodium (5.36 g, 0.233 mol) was dissolved in ethanol (absolute, 670 ml) and the solution was cooled to 10°. Tetraethyl 1-pentene-1,1,3,3-tetracarboxylate (83.4 g, 0.233 mol) in ethanol (absolute, 670 ml) was added over 30 min with the temperature maintained between 6 and 10° (immersion in an ice bath), and a deep yellow color appeared. The reaction mixture was stirred for 20 hr at 10° and then poured into chloroform (500 ml) and shaken well with hydrochloric acid (0.6 N, 375 ml). The aqueous layer was extracted with chloroform (3 × 200 ml) and the combined chloroform layer was washed with saturated salt solution (3 × 250 ml), dried, and evaporated under reduced pressure to give a yellow oil (57.5 g). Glc [column, 3% QF_1 on Chromosorb W (60–80 mesh), 5 ft × 0.125 in., Pyrex; flow rate, 12 ml/min; temperature, initial 80°, final 215°, at an average of 3.75° per minute] showed diethyl ethylmalonate (appearance temperature 117–120°) and three peaks with an appearance temperature around 170° in the ratio of 28:26:64. Diethyl ethylmalonate was removed by fractional vacuum distillation and the mixture of isomers of triethyl 3-ethyl-1(2)-pentene-1,1,3-tricarboxylate (**3a**) was used as such for the next step.

Diethyl 3-Ethyl-5,6-dihydro-2*H*-pyran-2-one-5,5-dicarboxylate (2).—Sodium ethoxide (60 mg), triethyl 3-ethyl-1(2)-pentene-1,1,3-tricarboxylate (7.68 g), and paraformaldehyde (0.801 g) were heated to 97° over 60 min (the reaction mixture becoming clear at about 80°) and then maintained at 97° for 3.25 hr. The mixture was cooled and dissolved in ether (50 ml), and the ethereal solution was washed with dilute hydrochloric acid (1 N, 3 × 10 ml) and water (2 × 10 ml), dried, and evaporated under reduced pressure to give an oil (5.96 g). Chromatography on 24 g of silica gel (Merck 0.05–0.2 mm) gave diethyl 3-ethyl-5,6-dihydro-2*H*-pyran-2-one-5,5-dicarboxylate (**2**) (2.15 g) as a colorless oil, eluted with ligroin–benzene (4:1). The nmr spectrum showed δ 1.11 (3 H, triplet, J = 7.4 Hz), 1.28 (6 H, triplet, J = 7.0 Hz), 2.40 (2 H, doublet of quartets, J = 7.4, 7.4, 7.4, 1.4 Hz), 4.26 (4 H, quartet, J = 7.0 Hz), 4.69 [2 H, narrow signal showing small (0.8 Hz) splitting], 6.71 ppm (1 H, narrow signal, $W_{1/2}$ = 3.6 Hz).

Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.98; H, 6.88.

The mass spectrum showed m/e (rel intensity at 70 and 12 eV, respectively) 271 (M + 1, 13, 2), 270 (M, 1.5, 4), 226 (10, 27), 198 (100, 100), 180 (27, 26), 170 (25, 7), 169 (19, 3), 152 (94, 25), 151 (38, 0), 125 (83, 6), 124 (30, 2); M^+ at 173.3 (calcd for 226 → 198, 173.5), 163.5 (198 → 180, 163.6), 146.0 (198 → 170, 145.9), 143.5 (226 → 180, 143.4), 128.3 (180 → 152, 128.3), 106.8 (270 → 170, 107.0), 101.5 (152 → 124, 101.2).

Further elution of the column gave **diethyl 5-ethyl-5,6-dihydro-2H-pyran-2-one-3,5-dicarboxylate (4, 0.42 g)** as a colorless oil. The nmr spectrum showed δ 0.98 (3 H, triplet, J = 7.2 Hz), 1.23 (3 H, triplet, J = 7.0 Hz), 1.35 (3 H, triplet, J = 7.0 Hz), 1.88 (2 H, quartet, J = 7.2 Hz), 4.0–4.5 (6 H, complex multiplet), 7.75 ppm (1 H, singlet).

Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.65; H, 6.78.

Diethyl 5-Ethyl-3,4-epoxytetrahydro-2*H*-pyran-2-one-3,5-dicarboxylate (5).—A suspension of peroxydisuccinic acid[9] (135 mg) in water (1 ml) was heated and stirred at 50° for 1 hr. The resulting aqueous solution was cooled to 42° and diethyl 5-ethyl-5,6-dihydro-2*H*-pyran-2-one-3,5-dicarboxylate (**4**) (135 mg) was added. The reaction mixture was stirred at 42° for 8 hr, cooled to about 10°, neutralized with sodium bicarbonate, and extracted with ether. The ethereal solution was washed with water (2 × 10 ml), dried, and evaporated under reduced pressure to give a quantitative yield of diester **5**. Recrystallization from ligroin gave colorless crystals: yield 43 mg; mp 50–51°; glc [column, 5% SE-30 on Chromosorb W (60–80 mesh), 5 ft × 0.125 in., stainless steel; temperature, −178°; flow rate, 10 ml/min] retention time 10.5 min relative to starting material 9.5 min. The glc of the mother liquors showed only the one peak corresponding to the isolated solid. The mass spectrum showed a peak at m/e 286 (calcd for $C_{13}H_{18}O_7$, M^+ 286). The nmr spectrum showed δ 1.02 (3 H, triplet, J = 7 Hz), 1.32 (3 H, triplet J = 7 Hz), 1.33 (3 H, triplet, J = 7 Hz), 1.8 (2 H, quartet, J = 7 Hz, exhibiting further splitting), 4.0–4.6 ppm (7 H, complex multiplet).

Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.40; H, 6.27.

Registry No.—**2**, 34993-71-0; **4**, 34993-72-1; **5**, 34993-73-2; tetraethyl 1-pentene-1,1,3,3-tetracarboxylate, 34993-74-3.

(10) This removal of a quantity of the solvent was necessary to ensure optimization of the ethylation reaction; otherwise, unethylated material was obtained, as the pyrone, ethyl 6-ethoxy-2*H*-pyran-2-one-3,5-dicarboxylated, *via* elimination of ethanol from tetraethyl 1-propene-1,1,3,3-tetracarboxylate. See M. Guthzeit and O. Dressel, *Ber.*, **22**, 1413 (1889).

Catalytic Deoxygenation of Organic Compounds by Carbon Monoxide. II.[1] Direct Synthesis of Schiff Bases from Aromatic Nitro Derivatives, Aldehydes, and Carbon Monoxide

ABUL F. M. IQBAL

Monsanto Research S.A., Eggbühlstrasse 36, 8050 Zürich, Switzerland

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The subject of the present communication is a novel synthesis of Schiff bases by intercepting *in situ* deoxygenated nitro derivatives by aldehydes. Thus, in the presence of a group VIII metal catalyst (*e.g.*, rhodium carbonyl), the interaction of benzaldehyde and aromatic nitro compounds under a pressure of

(1) For part I, see A. F. M. Iqbal, *Tetrahedron Lett.*, 3385 (1971).

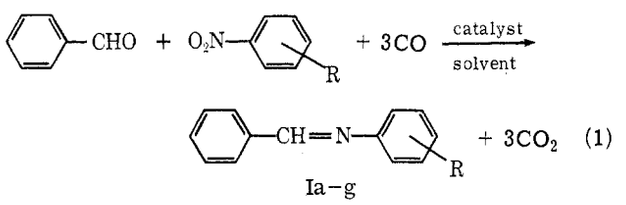
TABLE I

SCHIFF BASES BY THE CATALYTIC CONVERSION OF BENZALDEHYDE AND AROMATIC NITRO COMPOUNDS IN THE PRESENCE OF CARBON MONOXIDE[a]

					Physical constants[f]			
					Ir ($\nu_{C=N}$), μ[d]	^{1}H Nmr chemical shift, δ, ppm[e]		
Schiff base	R =	Yield, %[b]	Bp, °C (Torr)[c]	Mp, °C[c]		CH=N	Aromatic	CH_3
Ia	H	80	88–92 (0.3)	48–49	6.15	8.28	6.9–8.0	
Ia	H	6[g]	88–92 (0.3)	48–49	6.15	8.28	6.9–8.0	
Ia	H	78[h]	88–92 (0.3)	48–49	6.15	8.28	6.9–8.0	
Ib	*p*-OCH_3	60		71–72	6.15	8.30	6.65–7.95	3.70
Ic	*p*-$N(CH_3)_2$	65		98–99	6.19	8.37	6.5–7.95	2.93
Id	*o*-CH_3	82	94–98 (0.4)		6.12	8.17	6.6–7.95	2.32
Ie	*m*-CH_3	85	90–93 (0.3)		6.15	8.25	6.7–7.95	2.31
If	*p*-CH_3	83	97–100 (0.3)		6.14	8.24	6.8–7.9	2.26
Ig	*p*-Phenyl	84		147	6.16	8.41	7.05–8.05	

[a] Constant conditions: 0.1 mol benzaldehyde, 0.11 mol nitro derivative, 10^{-5} mol hexarhodium hexadecacarbonyl, 50 ml pyridine (solvent), 150 atm carbon monoxide (initial pressure at room temperature), 170°, 3 hr, 0.5-l. rocking stainless steel autoclave. [b] Based on benzaldehyde. [c] Boiling and melting points are uncorrected. [d] Liquids were measured neat, solids in chloroform. [e] Nmr spectra were taken in carbon tetrachloride. [f] Observed physical constants are identical with those of authentic samples, easily synthesized by applying the standard procedure [see, for example, A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p 653] for condensation of aldehydes with corresponding amines. [g] Yield obtained on substituting pyridine by 50 ml of benzene. [h] In dry *N*-methylpyrrolidine as solvent (at 70°, 50 atm, 6 hr).

carbon monoxide eventuated in the formation of the corresponding azomethines in high yields (eq 1).



Ia–g (1)

Carbon monoxide apparently functions here solely as a deoxygenating agent. All reactions were carried out in a stainless steel autoclave, using dry pyridine as solvent and hexarhodium hexadecacarbonyl as catalyst. The Schiff bases were obtained by fractional distillation or, where necessary, by fractional crystallization of the pyridine-free reaction mixture. The identity of the azomethine compounds has been ascertained by derivatization, as well as by ir and nmr spectroscopic comparison with authentic samples.

Some results and reaction conditions have been summarized in Table I. Only 5–7% Schiff base formation takes place in benzene, while over 80% yield of the same is obtained in pyridine solvent. Anhydrous *N*-methylpyrrolidine, for example, enables successful operation under essentially mild conditions (70°, 50 atm CO). Analogous enhancement of the catalytic activity of rhodium carbonyls by the addition of tertiary amines has been noted previously.[1]

Azomethine yields from dimethylamino- and methoxy-substituted nitrobenzenes are distinctly lower. However, in view of the paucity of data and manipulative losses, particularly during work-up of the latter compounds, substituent effects are not easy to interpret. Some trends may seem apparent; nonetheless, it would be premature to make any generalizations. While exclusively rhodium carbonyl has been listed in Table I, under analogous conditions, iron pentacarbonyl, triruthenium dodecacarbonyl, and dicobalt octacarbonyl likewise catalyze the formation of Schiff base by the present route. In the absence of any one of these metals, no formation of the corresponding azomethine derivative was observed under the given conditions.

A reasonable explanation for Schiff bases would be eq 2. This is unlikely, since intermediacy of amines is

$$ArNO_2 \longrightarrow ArNH_2 \xrightarrow{PhCHO} ArN{=}HCPh \qquad (2)$$

precluded by the absence of water[1] or of sufficiently high pressures of hydrogen.[2] The formation of aryl isocyanate by reductive carbonylation[5] of aromatic nitro compounds would, on the other hand, suggest the following route[6] (eq 3).

$$ArNO_2 \longrightarrow ArNCO \xrightarrow{PhCHO} ArN{=}HCPh \qquad (3)$$

However, control experiments with nitrobenzene and ethanol, in place of benzaldehyde, under conditions of azomethine formation yielded but small amounts of the corresponding urethane (<10%) and urea (<5%) derivatives. The major product, as expected,[1] was aniline (*ca.* 45%), which could not have originated in phenyl isocyanate since no water was present. While consequently the isocyanate route (eq 3) may at best account for a minor portion of Schiff base, we believe that the preponderant mechanism incorporates the following sequence of reactions.

$$ArNO_2 + 2CO \xrightarrow{\text{Catalyst}} [Ar\text{-}\underline{N}] + 2CO_2$$
II

$$II + Ar'CHO \longrightarrow Ar'CH(O)NAr$$
IIIa

$$Ar'CH{=}NAr \rightleftharpoons Ar'CH(O)NAr$$
IIIb

$$III + CO \longrightarrow Ar'CH{=}NAr + CO_2$$

(2) At low partial pressures of hydrogen the corresponding 1,3-diarylureas are formed[3,4] along pathways independent of intermediate amine.

(3) A. F. M. Iqbal, submitted for publication.

(4) F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970).

(5) W. B. Hardy and R. P. Bennett, *Tetrahedron Lett.*, 961 (1967).

(6) H. Staudinger and R. Endle, *Ber.*, **50**, 1042 (1917).

The first step is considered to involve the catalytic deoxygenation of the nitro compound to a nitrene (II), discrete or complexed, whose subsequent addition to the carbonyl compound, present in solution, would furnish the oxazirane IIIa, and correspondingly the isomeric nitrone IIIb.

The intermediacy of nitrene and nitrenoid intermediates has been invoked by previous investigators[4,7,8] in an attempt to rationalize the formation of an array of products from catalytic coversions of nitro compounds with carbon monoxide. Even in formation of isocyanates,[5] nitrene intervention is made very probable by the analogous reaction of azides.[9] One might thus expect *in situ* trapping of the reactive intermediate by aldehyde (*vide supra*) to prevail over transformation to isocyanate and subsequent reaction (eq 3). As additional persuasive evidence for the first two steps may be cited the formation of Schiff bases by thermolysis of phenyl azide in aldehydes or ketone, reported by Neiman, *et al.*[10,11] The expected nitrone or oxazirane, however, remained elusive in these latter reactions. This fact is ascribed by the authors to probable oxidation of excess carbonyl compound by the oxygenated intermediates, which in the process become reduced to Schiff base.

Once formed, III can be reduced by carbon monoxide in the presence of rhodium carbonyl to the Schiff base I, as could also be verified experimentally.[12]

Experimental Section

Materials.—Commercial carbon monoxide was used without further purification. Benzaldehyde and various nitro compounds were freshly distilled prior to reaction. Hexarhodium hexadecacarbonyl was prepared by the reductive carbonylation of rhodium chloride in the presence of iron pentacarbonyl.[14] Pyridine and *N*-methylpyrrolidine were additionally dried and distilled over potassium hydroxide. Authentic samples of Schiff bases for comparison of physical constants were synthesized by usual condensation[2] of benzaldehyde with corresponding amines.

General Procedure for Schiff Bases.—All reactions were carried out in a stainless steel autoclave of 500-ml capacity, heated by an external rocking electric oven. Only one experiment, with benzaldehdye and *p*-nitrobiphenyl, will be described here to exemplify the general procedure adopted; the effect of varying conditions can be seen from the data presented in Table I. A solution of benzaldehyde (0.1 mol), *p*-nitrobiphenyl (0.11 mol), and hexarhodium hexadecacarbonyl (10^{-5} mol) in 50 ml of anhydrous pyridine was allowed to react with carbon monoxide (150 atm). The content of the autoclave was heated during 40 min to 165–170° and held at this temperature for 3 hr. After cooling, the autoclave was discharged and pyridine was evaporated from the mixture under vacuum. The residue was swirled with *ca.* 40–50 ml of methanol and filtered to give in 84% yield substantially pure crystals of *N*-benzylidene-*p*-phenylaniline (Ig), mp 147°. Identity of the compound was confirmed by mixture melting point, ir, and nmr spectroscopic comparison with an authentic sample. Yields and physical properties of further azomethine derivatives are compiled in Table I.

(7) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).
(8) T. Kajimoto and J. Tsuji, *Bull. Chem. Soc. Jap.*, **42**, 827 (1969).
(9) R. P. Bennett and W. B. Hardy, *J. Amer. Chem. Soc.*, **90**, 3295 (1968).
(10) L. A. Neiman, V. I. Maimind, and M. M. Shemyakin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1498 (1962).[11]
(11) Compare also *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1831 (1964).
(12) For example, α-phenyl-*N*-phenylnitrone[13] was smoothly deoxygenated by hexarhodium hexadecacarbonyl at 150° and 130 atm carbon monoxide pressure to *N*-benzylideneaniline.
(13) O. H. Wheeler and P. H. Gore, *J. Amer. Chem. Soc.*, **78**, 3363 (1956).
(14) B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, and R. N. Haszeldine, *J. Organometal. Chem.*, **14**, 417 (1968).

Registry No.—Ia, 538-51-2; Ib, 783-08-4; Ic, 889-38-3; Id, 5877-55-4; Ie, 5877-58-7; If, 2272-45-9; Ig, 13924-28-2; carbon monoxide, 630-08-0.

Conformational Preference of *cis*-8-Oxabicyclo[4.3.0]non-3-ene

BRADFORD P. MUNDY,* KAUO-RONG SUN, AND RODNEY D. OTZENBERGER[1]

Department of Chemistry, Montana State University, Bozeman, Montana 59715

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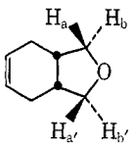
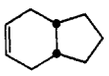
cis-8-Oxabicyclo[4.3.0]non-3-ene (**1**) has found occasional use as a model of *cis*-bicyclo[4.3.0]non-3-ene (**2**), primarily due to the ease of preparing **1**.[2] As part of our effort to test the validity of using an oxygen-containing molecule as a model for its carbocyclic analog,[3] we examined the ground-state conformation of **1**.



1



2

Using results based on the steric course of epoxidation, previous investigations have suggested that **5** is the preferred ground-state conformer of **2**[4] (Scheme I[5]). We have examined the products from epoxidation of **1** and find a fortuitously similar product ratio (Scheme I). These data would appear to support, based on steric data alone, conformer **8** as the ground-state conformer. Furthermore, this would be consistent with the steric course of oxymercuration and the oxygen participation noted for this reaction.[6] However, the nmr spectrum of **1** is better accommodated by conformer **9**.

The spectrum of **1** exhibited a multiplet for the pro-

(1) NDEA Predoctoral Fellow, 1968–1971. Abstracted, in part, from the Ph.D. Thesis of Rodney D. Otzenberger, Montana State University, 1971.
(2) (a) E. L. Eliel and C. Pillar, *J. Amer. Chem. Soc.*, **77**, 3600 (1955); (b) B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).
(3) (a) B. P. Mundy, A. R. DeBernardis, and R. D. Otzenberger, *ibid.*, **36**, 3830 (1971); (b) B. P. Mundy and R. D. Otzenberger, *ibid.*, **37**, 677 (1972).
(4) J. C. Jallageas and E. Casadevall, *C. R. Acad. Sci., Ser. C*, **268**, 449 (1969).
(5) We did not analyze the epoxides, but rather compared the alcohols resulting from lithium aluminum hydride reduction of the epoxide mixture. The stereochemistry of the alcohols had been previously assigned,[3b] and the known stereospecificity of reductive opening of the epoxide moiety assured us that we were analyzing an alcohol mixture representative of the epoxide mixture.
(6) See ref 3b. The stereospecificity and oxygen participation is best explained by invoking an intermediate for reactions proceeding *via* carbonium ion intermediates.