

hydrate in 10 mL of MeOH. The precipitate was filtered off and recrystallized from MeOH.

Workup of Reaction Mixture of 3-(1,4-Cyclohexadienyl)-L-alaninol (8). After reduction of 9.80 g (40 mmol) of 7-HBr²⁰ according to method A, NH₃ was evaporated, and the residue dissolved in water was extracted with EtOAc. The organic solvent was removed, and the residue crystallized in ether was diluted with diisopropyl ether, resulting in 4.45 g (72.3%) of 8: IR (KBr) 3355 and 3270 (NH₂), 3150 (br) and 1056 (OH), 1593 (C=C), 1428, 962, 658 cm⁻¹, no peak characteristic to aromatic ring; ¹H NMR (CDCl₃) δ 1.75–2.25 (m, 5 H, NH₂ + OH + γ-CH₂), 2.65 (m, 4 H, 3',6'-CH₂) 3.0 (m, 1 H, β-CH), 3.3 and 3.6 (AB q, 2 H, α-CH₂), 5.5 (br, 1 H, 2'-CH), 5.7 (d, 2 H, 4',5'-CH); ¹³C NMR (CDCl₃) δ 26.90 and 29.13 (3',6'-CH₂), 42.44 (γ-CH₂), 50.1 (β-CH), 66.55 (α-CH₂), 121.58 (2'-CH), 124.14 and 124.25 (4',5'-CH), 131.95 (1'-C). The structure of 8 is proved by these data and the UV spectra, where the conjugation of double bonds was excluded. 8 is not stable in the ambient atmosphere and slowly turns yellow.

To a solution of 4.0 g (26.0 mmol) of 8 in 50 mL of EtOAc was added 3.5 g (30.0 mmol) of maleic acid in EtOAc (50 mL)–EtOH (10 mL), resulting in 6.93 g of the hemimaleate salt of 8, mp 137–138 °C. An analytical sample was recrystallized from EtOH: mp 138–139 °C; [α]_D²⁵ +5.95° (c 1.08; EtOH); ¹H NMR (Me₂SO-*d*₆/CDCl₃) δ 2.23 (d, 2 H, γ-CH₂), 2.63 (br, 4 H, 3',6'-CH₂), 2.9–3.3 (m, 1 H, β-CH), 3.56 (m, 2 H, α-CH), 5.56 (br, 1 H, 2'-CH), 5.68 (br s, 2 H, 4',5'-CH), 6.13 (s, 2 H, maleic CH=CH), 5.8–8.8 (br, 5 H, NH₃⁺ + OH + CO₂H); mass spectrum, *m/e* (relative intensity) 152.107 (M – H, 0.8), 122 (4.3), 105 (4.5), 91 (6.5), 79 (5.5), 77 (4.3), 72 (6.2), 60.046 (100).

To the mother liquor of 4.45 g of 8 was added 1.20 g of maleic acid dissolved in EtOAc (20 mL)–EtOH (5 mL), resulting in a yellowish product: 2.15 g; mp 142–143 °C. Recrystallization from EtOH (15 mL) gave a mixture (about 1:1) of 8 (M₂) and 3-(cyclohexen-1-yl)alaninol (18, M₁) as hemimaleate salts: yield 0.73 g; mp 147–149 °C; [α]_D²⁵ 0° (c 1.0, EtOH); IR (KBr) 3550–2200 (CO₂H), 1046 (OH), 1353, 1192, 957, 888, 864, 758, 703 cm⁻¹; ¹H NMR (KBr) δ 1.6 (br, 2 H) and 1.9 (br, 2 H) for 4'- and 5'-CH₂ in addition to the ¹H NMR spectrum of the hemimaleate salt of 8 with broader peaks; mass spectrum, *m/e* (relative intensity) 155 (M₁, 0.1), 152 (M₂ – H, 0.5), 124 (M₁ – 31, 10), 122 (M₂ – 31, 3.5), 81 (8), 79 (7), 60 (100).

Workup of Reduction Mixture of Boc-Lys-NH₂ (11). After reduction of 2.35 g (7.0 mmol) of 11 according to method A, NH₃ was evaporated, and the residue was washed with EtOH. The TLC picture of this solution was very heterogeneous. The presence of 17 (*R*_f¹ 0.70), 12 (*R*_f⁴ 0.40), 11 (*R*_f⁴ 0.35), and 13 (*R*_f⁴ 0.08) was detected. The filtrate was evaporated, and ether was decanted from the residual oil. From this ethereal solution was isolated 17: 0.12 g (14.6 %); mp 101–104 °C.

The residue of the original oil was chromatographed on a silica gel column by using solvent system 4. Because of poor resolution 13 was the only product isolated in a pure state: yield 0.20 g (22 %); mp 131–136 °C; IR (KBr) 1650 (CO) cm⁻¹, no urethane; ¹H NMR (Me₂SO-*d*₆/CDCl₃) δ 1.5 (br, 6 H, β-, γ-, δ-CH₂), 2.1 (t, 2 H, α-CH₂), 2.65 (t, 2 H, ε-CH₂), 6.7 and 7.4 (br, 2 H, CONH₂), 7.7 (br, 2 H, NH₂). For confirmation of the structure, 13 was acylated with Boc₂O in the usual manner,¹⁶ resulting in 16 which was identified by TLC, melting point, and IR and ¹H NMR spectra.

Workup of Reduction Mixture of Boc-Lys(Boc)-NH₂ (14). After evaporation of NH₃ the residue was extracted with EtOAc. Column chromatography on silica gel, by using EtOAc and solvent system 3, resolved 40.5% of 15 as an oil [TLC *R*_f² 0.65; IR (film) 1685 (urethane), 1065 (OH), no amide; ¹H NMR (CDCl₃) δ 1.43 and 1.2–1.9 (s + m, 24 H, 2 *t*-Bu and γ-, δ-, ε-CH₂), 3.05 (m, 2 H, ζ-CH₂), 3.5 (m, 3 H, α-CH₂ + β-CH), 3.8 (br, 1 H, OH), 5.2 (m, 2 H, 2 NH) and 3.6% of 16. The other products of the reductions with methods A and B could not be completely resolved.

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Registry No. 1, 7536-55-2; 2-DCHA, 63491-82-7; L-3, 13726-85-7; DL-3, 85535-45-1; L-4-DCHA, 85535-46-2; DL-4-DCHA, 85535-48-4; 5, 7324-05-2; 6-hemioxalate, 85535-49-5; 7, 5241-58-7; 7-HBr, 24730-33-4; 8, 85535-50-8; 8-hemimaleate, 85535-51-9; 9, 74244-17-0; 10-DCHA, 85535-52-0; 11-hemioxalate, 85535-53-1; 12, 85535-54-2; 13, 373-04-6; 14, 55592-82-0; 15, 85535-55-3; 16, 85535-56-4; 17, 4248-19-5; 18-hemimaleate, 85535-58-6; 19, 55592-81-9; 20, 85535-59-7; Boc-Lys(Z)-OPfp, 50903-59-8; Boc-Lys(Boc)-OH, 2483-46-7; ε-[(*tert*-butoxycarbonyl)amino]caproic acid-DCHA salt, 85535-60-0; ε-aminocaproic acid, 60-32-2; sodium, 7440-23-5; ammonia, 7664-41-7.

Sunlamp-Irradiated Phase-Transfer Catalysis. 2.¹ Cobalt Carbonyl Catalyzed Carbonylation of Benzyltriethylammonium or Allyltriethylammonium Halides under 1 atm of Carbon Monoxide

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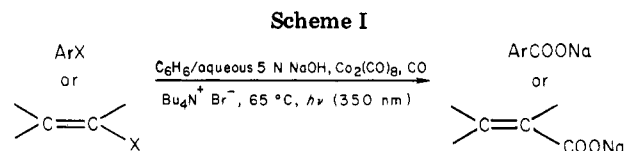
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In a previous publication,² we have shown for the first time that cobalt-catalyzed carbonylation (1 atm of CO) of aryl and vinyl halides can be easily achieved provided that the reaction medium is irradiated. These reactions were performed under photostimulated (350 nm in a Rayonet device) phase-transfer-catalysis (PTC) conditions (C₆H₆/aqueous NaOH) in the presence of catalytic amounts of both Co₂(CO)₈ and Bu₄N⁺Br⁻ (Scheme I). The corresponding acids were obtained in high yields.

Since these first results, we have been able to show that simple irradiation through Pyrex flasks with an inexpensive commercial sun lamp is sufficient to perform these reactions.^{1,3} Moreover, we also showed that a number of these reactions might be performed in aqueous sodium hydroxide, i.e., without an organic solvent.¹

Numerous arguments support a S_{RN}1 type mechanism (Scheme II)¹ between the aryl (or vinyl) halide and Co(CO)₄⁻ generated in situ from Co₂(CO)₈.⁵



Of course, most of these carbonylations necessitated the use of an ammonium salt as phase-transfer catalyst. During the preliminary study of the influence of the structure of the ammonium salt on the course of the carbonylation, we observed that under the above conditions, benzyltriethylammonium chloride was easily carbonylated

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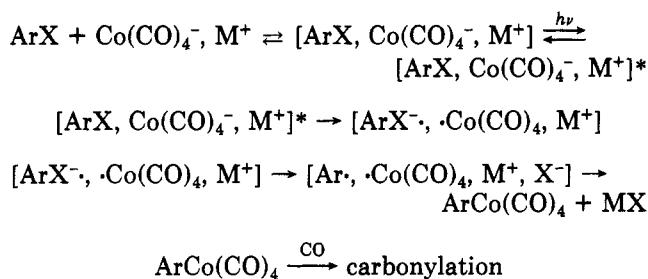
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Table I. Carbonylation of Benzyl- and Allyltriethylammonium Halides

$\text{RCH}_2\text{NEt}_3^+, \text{X}^- \xrightarrow{a} \text{RCH}_2\text{COOH}$				
R	X	conditions ^a	acid	isolated yield, %
C_6H_5	Br	A; B	$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	80; 85
C_6H_5	Cl	A; B	$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	85; 85
$2\text{-CH}_3\text{C}_6\text{H}_4$	Br	A; B	$2\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$	85; 85
$2\text{-CH}_3\text{C}_6\text{H}_4$	Cl	A; B	$2\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$	85; 85
$4\text{-CH}_3\text{C}_6\text{H}_4$	Br	A; B	$4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$	85; 85
$3\text{-CH}_3\text{C}_6\text{H}_4$	Cl	B	$3\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$	83
$4\text{-ClC}_6\text{H}_4$	Cl	A; B	$4\text{-COOHC}_6\text{H}_4\text{CH}_2\text{COOH}$	70; 75
$4\text{-BrC}_6\text{H}_4$	Br	A; B	$4\text{-COOHC}_6\text{H}_4\text{CH}_2\text{COOH}$	75; 80
$2\text{-BrC}_6\text{H}_4$	Br	B	$2\text{-COOHC}_6\text{H}_4\text{CH}_2\text{COOH}$	78
$4\text{-CNC}_6\text{H}_4$	Br	B	$4\text{-COOHC}_6\text{H}_4\text{CH}_2\text{COOH}$	85
$\text{CH}_2=\text{CH}$	Br	B	$\text{CH}_2\text{CH}=\text{CHCOOH}$ (trans)	80
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$ (trans)	Cl	A	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{COOH}$ (trans)	70

^a Reactions were carried out by using the following reactants ratio: ammonium salt/ $\text{Co}_2(\text{CO})_8 = 20:1$ mmol in either condition A [$(\text{C}_6\text{H}_6, 25 \text{ mL})/\text{aqueous } 5 \text{ N NaOH} (50 \text{ mL})$] or B (aqueous 5 N NaOH (50 mL)) at 65 °C (overnight) under a slow stream of carbon monoxide and under photostimulation with the sun lamp.

Scheme II



to phenyl acetic acid.² Examination of the literature showed that carbonylation of benzyltrialkylammonium halides might take place under certain conditions. Thus, Alper et al.⁶ have demonstrated the stoichiometric carbonylation of such benzylammonium halides by acetyl-cobalt tetracarbonyl generated from CH_3I and $\text{Co}(\text{CO})_4^-$ under PTC conditions. These authors suspected the intervention of benzyl radicals during these reactions.⁶

This suggestion as well as our observations (vide supra) led us to conjecture that the photostimulated $\text{S}_{\text{RN}}1$ conditions^{1,2} might be convenient for performing catalytic carbonylation of benzyltrialkylammonium halides. As we show below, this expectation has been completely verified, and we present here the first catalytic carbonylation of benzyl- (and allyl-)triethylammonium salts.

First of all, control experiments performed on benzyltriethylammonium chloride indicated that in the absence of irradiation, only traces of phenylacetic acid were formed (65 °C, 24 h). This result confirms literature data⁶ but shows that such ammonium salts are not completely inert toward $\text{Co}(\text{CO})_4^-$ under PTC conditions. In any case, photostimulation appeared essential for performing the carbonylation of benzyltriethylammonium halides.

Results obtained with some representative ammonium salts have been reported in Table I. As may be seen, these reactions may be performed in either of the conditions A or B (for definition, see footnote a of the Table) and afford the corresponding acids in 75–85% yield. As expected, nitrile groups on the aromatic ring were transformed into carboxylic functions due to the hydrolyzing conditions used. Benzylammonium salts bearing a halogen (Br or Cl) on the aromatic nucleus were carbonylated to diacids as expected from our result on the carbonylation of (*p*-chlorophenyl)acetic acid.¹

Finally, allyltriethylammonium halides were also carbonylated in good yields. Note that unless the carbon-carbon double bond was conjugated with an aromatic ring, isomerization took place during the reaction, thus leading to α,β -unsaturated acids.

Last, we briefly examined the possible catalytic carbonylation of benzyl halides themselves under irradiated PTC conditions and in the presence of catalytic amounts of triethylamine ($\text{Et}_3\text{N}/\text{halide} = 0.1$). In fact, it was found that the carbonylation yields strongly depended on the structure of the benzyl halides. For instance, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, and *p*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Br}$ (20 mmol) were carbonylated ($\text{Co}_2(\text{CO})_8/\text{halide} = 0.05$) to the corresponding acids in high yields (85%, 2 h; 85%, 6.5 h; 80%, 2 h, respectively). However, carbonylation of *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Br}$ led to the corresponding acid in only a 25% yield (5 h) due to the formation of several nonacidic byproducts.

In conclusion, the reactions described in this paper constitute the first catalytic carbonylation of benzyl- and allyltrialkylammonium halides. It must be noted that for some benzyltriethylammonium halides acid yields are higher than those reported for the carbonylation of the corresponding benzyl halides with either $\text{Co}_2(\text{CO})_8$ or $\text{Co}(\text{CO})_3\text{NO}$ under PTC conditions.^{7,8}

Experimental Section

Materials. Benzyl- (or allyl-)trialkylammonium halides were either commercial or prepared by standard procedures.⁹ Dicobalt octacarbonyl was purchased from Fluka and was used without further purification. Carbon monoxide N_2O (L'Air Liquide) was used.

General Procedures. IR spectra were recorded with a Perkin-Elmer spectrophotometer (Model 580 B). NMR spectra were recorded on a Perkin-Elmer R 12 B instrument. The sun lamp used was purchased from Philips. It was equipped with a Philips 13178 HPQ 125-W lamp (main emissions at 300, 315, 365, 405, and 435 nm). All the compounds prepared in this work were identified by comparison (melting point, IR, NMR) with authentic samples.

Carbonylation Procedure. Carbonylations were carried out in Pyrex flasks irradiated by means of the sun lamp either under PTC conditions ($\text{C}_6\text{H}_6/\text{aqueous } 5 \text{ N NaOH}$) or in aqueous 5 N NaOH. The typical procedure is exemplified for the carbonylation of benzyltriethylammonium bromide. To a 250-mL Pyrex flask

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were added aqueous 5 N sodium hydroxide (50 mL), $\text{Co}_2(\text{CO})_8$ (1 mmol), and benzyltriethylammonium bromide (20 mmol). The reaction mixture was then heated to 65 °C under a slow stream of carbon monoxide (heating was assured by the IR device of the sun lamp). Irradiation was achieved with the sun lamp placed about 30 cm from the flask. After stirring overnight under these conditions, classical workup afforded pure phenylacetic acid (85% yield).

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Registry No. $\text{PhCH}_2\text{NEt}_3^+\text{Br}^-$, 5197-95-5; $\text{PhCH}_2\text{NEt}_3^+\text{Cl}^-$, 56-37-1; 2- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Br}^-$, 85267-31-8; 2- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Cl}^-$, 85267-32-9; 4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Br}^-$, 85267-33-0; 3- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Cl}^-$, 85267-34-1; 4- $\text{ClC}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Cl}^-$, 5197-90-0; 4- $\text{BrC}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Br}^-$, 85267-35-2; 2- $\text{BrC}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Br}^-$, 85267-36-3; 4- $\text{CNC}_6\text{H}_4\text{CH}_2\text{NEt}_3^+\text{Br}^-$, 85267-37-4; $\text{CH}_2=\text{CHCH}_2\text{NEt}_3^+\text{Br}^-$, 29443-23-0; (*E*)- $\text{PhCH}=\text{CHCH}_2\text{NEt}_3^+\text{Cl}^-$, 85267-38-5; PhCH_2COOH , 103-82-2; $\text{Co}_2(\text{CO})_8$, 10210-68-1; 2- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$, 644-36-0; CO , 630-08-0; 4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$, 622-47-9; 3- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$, 621-36-3; 4- $\text{HOOC}_6\text{H}_4\text{CH}_2\text{COOH}$, 501-89-3; 2- $\text{HOOC}_6\text{H}_4\text{CH}_2\text{COOH}$, 89-51-0; (*E*)- $\text{CH}_3\text{CH}=\text{CHCOOH}$, 107-93-7; (*E*)- $\text{PhCH}=\text{CHCH}_2\text{COOH}$, 1914-58-5.

A Comparison of the Regioselectivity in the Enol Acetate Formation and the Vilsmeier-Haack Reaction of Some Methyl-Substituted Cycloalkanones

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Substituted cycloalkanones are of great importance as starting materials and building blocks in organic synthesis. Unsymmetrically substituted cycloalkanones introduce an element of selectivity between two nonequivalent α -positions (α and α'), and isomeric mixtures may result when such compounds participate in a chemical reaction.

The Vilsmeier-Haack reaction of cycloalkanones^{2,3} (also known as chloroformylation) leads to β -chlorovinyl aldehydes 1, which are interesting intermediates that lend themselves to further useful elaborations.^{4,5}

Although a number of cyclic β -chlorovinyl aldehydes has been prepared,^{2b,4} the problem of regiochemistry in the reaction between unsymmetrically substituted alicyclic ketones and the Vilsmeier-Haack reagent has not been much discussed.⁶

In the Vilsmeier-Haack reaction the enol form of the ketone is thought to be attacked by the electrophile, the chloro(dimethylamino)methyl cation, formed from di-

methylformamide and phosphoroylchloride.² Ketones forming two different enols should give rise to two products, and we became interested in how a small substituent such as the methyl group in the β -position of cyclic ketones would affect the product distribution by steric interaction. Work along these lines has only rarely been reported.⁷

We now report our results on the regiochemistry of the chloroformylation of some methyl cycloalkanones using the dimethylformamide- POCl_3 reagent in trichloroethene.³

For comparison we determined the product distribution of the enol acetate formation under acidic conditions⁸ for the same methylcycloalkanones.

Results and Discussion

The methyl-substituted cycloalkanones 2, 7, 12, 17, and 22 were treated with a slight excess of the DMF- POCl_3 (1.3:1.1) reagent in trichloroethene at 55–60 °C for 3 h³ to give the chloroformylated derivatives shown in Table I, reaction A.

The enol acetates of the same ketones (except for 22) were prepared by isopropenyl acetate/*p*-toluenesulfonic acid treatment at 60–90 °C overnight.⁸ The results are shown in Table I, reaction B. When acetic anhydride was used instead of isopropenyl acetate in the case of 2, the GC yield was much lower (10% instead of 90%) but the relative ratio of enol acetates remained the same. When acetic anhydride was used in the case of 7, the ratio of the enol acetates was 66:34 as determined by ¹H NMR spectroscopy and 60:40 as determined by GC.⁹ Performing the reactions in trichloroethene as solvent did not alter the results.

The product distributions of reactions A and B were determined by GC analysis and ¹H NMR spectroscopy on the crude products.

Since the Vilsmeier-Haack reaction produced dark unknown side products, the crude products were not suitable for a direct NMR analysis and had to be distilled. This operation did not change the relative ratios of β -chlorovinyl aldehydes as could be seen by addition of $\text{Eu}(\text{fod})_3$ to the NMR samples. The formyl proton resonances separated completely, and integration gave the same ratio of isomers as the GC analyses. The structures of the products were determined by ¹H NMR spectroscopy and deserve some comments.

Information about the structures was obtained by examining the resonances of the allylic protons, which appeared as overlapping multiplets in the original spectra but were completely separated upon addition of $\text{Eu}(\text{fod})_3$. In each isomeric couple the isomer with the methyl group distant from the aldehyde group has four allylic protons, while the other one has only three, except for 23 and 24, which both have four. However, since 23 and 24 were formed in equal amount, the problem of differentiating between them did not arise in this context. Thus, by comparing the integrals and coupling patterns, structures 3, 4, 8, 9, 13, 14, and 18 were established.

The europium atom is assumed to coordinate to the oxygen atom of the aldehydes, which would shift the signals of the proximate methyl and allyl protons more downfield as compared to the distant ones. This was quite clear from the NMR spectra and provided additional structural evidence.

The structures of the enol acetates 5, 6, 15, 16, 20, and 21 were determined by ¹H NMR analysis on the crude

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