3-Alkoxyacroleins in Organic Synthesis

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3-Alkoxyacroleins are reviewed as useful C1 building blocks for cyclizations and C–C bond connections. They open pathways to a variety of heterocyclic systems with up to fourteen-membered rings and permit oxoprenylations of carbon nucleophiles, resulting in other versatile intermediates such as α,β-unsaturated aldehydes and 1-alkoxy-1,3-dienes.

1. Introduction

Carbon-13 chemical shifts of typical β-alkoxy-α,β-unsaturated aldehydes (3-alkoxyacroleins) such as 2-methyl-3-ethoxyacrolein 1 or 3,4-dihydro-2H-pyran-5-carbaldehyde 2 reflect a considerable electron deficiency at both the aldehyde and the enol ether carbon when compared with ethylformate 3 as reference compound.

1H-C-NMR: Values in ppm (J values in Hz)

Thus, 3-alkoxyacroleins can be considered as vinylogous formates and are expected to react as mono- and bifunctional electrophiles (electrocyclophiles). Thereby, they can be used in place of the unstable malonic dialdehdes and the corresponding less reactive tetraacetalts. Carbonyl reactions, vinylogous acylations, and cyclizations are possible. Furthermore, 3-ethoxyacroleins have been shown by NMR studies\(^1\) to equilibrate between the E,s-Z and the E,s-E conformations, in which not even bulky groups hinder the attack of nucleophiles at either of the electrophilic centers.

2. Synthesis of 3-Alkoxyacroleins

2.1. 3-Ethoxyacroleins

3-Ethoxyacroleins 1 are generally prepared in three steps from aldehyde diethylacetals 6, which can be obtained either by acetylation of aldehydes 4 or by reaction of alkylmagnesium halides 5 with triethylorthoformate. Elimination of ethanol in the presence of phosphoric acid or thermocatalytically\(^2,3\) affords alkynyl ethyl ethers 7. Addition of triethyl orthoformate catalyzed by boron trifluoride dietherate yields the 2-alkylmalonic dialdehyde tetraethylacetales 8, which are hydrolyzed in slightly acidic solution to the target ethoxyacroleins 1,2,3.

### Table: Yield [%] of (8 → 1)

<table>
<thead>
<tr>
<th>R'</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>95</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>90</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>85</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>90</td>
</tr>
<tr>
<td>n-C₆H₁₃</td>
<td>70</td>
</tr>
<tr>
<td>n-C₆H₁₃</td>
<td>90</td>
</tr>
</tbody>
</table>

2.2. 3-(Trimethylsilyloxy)acroleins

More reactive, and hence less stable, 3-(trimethylsilyloxy)acroleins 11 are obtained by reacting the sodium or potassium salts of malonic dialdehydes 9 with chlorotrimethylsilanes 10,4,5.
2.3. Heteroalicyclic 3-Alkoxycroclesins

3-Alkoxycroclesins containing the alkox group within a heterocyclic ring are expected to undergo useful ring-opening reactions upon nucleophilic addition. 3,4-Dihydro-2H-pyan-5-carbaldehyde 2, a versatile representative, can be prepared from 3,4-dihydro-2H-pyan 12. One method involves preparing a cycloaddition of ethyl trichloroacetate to yield 7,7-dichloro-2,3-oxabicyclo[4.1.0]heptane 13, which undergoes ring expansion in the presence of t-butoxide to give 2-t-butoxy-3-chloro-2,5,6,7-tetrahydroxepine 14. The latter undergoes ring contraction in acidic media to give the target compound 2. More conveniently, 2 can be prepared by direct Vilsmeier formation of 3,4-dihydro-2H-pyan 12. The best overall yield, however, is achieved by following the pathway outlined for 2-ethoxy-3-croclesins, involving 2-ethoxy-3-dioxine methyltetrahydro-2H-pyan 159,9 as heteroalicyclic malonic dialdehyde tetraacetate. The latter procedure was also successfully used to prepare dihydro-1,4-dioxine-3-carbaldehyde 10.

Aminolyis of 3,4-dihydro-2H-pyan-5-carbaldehyde (2) results in ring-opening to 2-(3-hydroxypropyl)-3-aminocroclesins 17 in ring-opening to 2-(3-hydroxypropyl)-3-aminocroclesins 17.

3-Amino-2-(3-hydroxypropyl)-crocleine (17; R = H): Concentrated aqueous ammonia (50 ml) is cooled to 5°C in an ice bath. After dropwise addition of 3,4-dihydro-2H-pyan-5-carbaldehyde (2; 1.1 g, 10 mmol), the yellow solution is stirred until the ice has melted. Concentration in vacuo (heated water bath kept below 40°C) yields an orange oil, which crystallizes overnight in the refrigerator. The yellow crystals are crushed in carbon tetrachloride, filtered by suction, washed with the same solvent and dried in vacuo; yield: 1.0 g (78%); m.p. 71°C.

3.2. Heterocyclizations with 3-Aminoacroleins

3.2.1. Pyridines

Cyclocondensation of 3-aminoacroleins 16a with 3-methylene-carbonyl compounds 18 such as β-diketones, β-oxoesters, and cycloalkanones affords substituted and fused pyridines 19.

3-Acetyl-2-methylpyridine 19 (R1 = H, R2 = CH3, R3 = COCH3)4

3-Aminoacroleins 16a (R1 = H, 4.15 g, 50 mmol), ammonium acetate (50 mg), and acetylene (18, R2 = CH3, R3 = COCH3, 6.0 g, 60 mmol) are refluxed for 12 h in an oil bath with temperature kept at 110°C. After cooling to room temperature, the brown oil is dissolved in ether (100 ml). The ether solution is dried with magnesium sulfate and filtered by suction. After removal of the ether, the residue is distilled under reduced pressure; yield: 3.4 g (50%); b.p. 104–105°C/16 mbar.

3.2.2. Pyrimidines

The primary amino group of 3-aminoacroleins 16a adds to phenylisocyanate (20a, X = O) to yield 3-(3-phenylenedioi)-acroleins (21, X = O).15 The same reaction with phenylisothiocyanate (20b, X = S)15 and diphenylcarbonicidime (20c, X = NC6H4)16 results in heterocyclization of the thiourea and guanidine intermediates to 1-phenylpyrimidin-2-(1H)-thiones 22 and 1-phenylpyrimidin-2-(1H)-pyrimidines 23.
3.3. Vinlylogous Vilsmeier Formylation

3-(N,N-Dimethylamino)-acroleins 16b as vinylogues of N,N-dimethylformamide can be used for vinylogous Vilsmeier formylations of nucleophilic aromatic rings such as N,N-dimethylaniline (24a) or N-methylpyrrole (24b). The corresponding α,β-unsaturated aldehydes 25 are obtained.

\[ \text{Ar-H} + (\text{CH}_3)_2\text{N}-\text{C} = \text{N} + \text{RCHO} \rightarrow \text{Ar}-\text{C} = \text{O} + (\text{CH}_3)_2\text{NH} \]

(\(E\))-3-(N-Methyl-2-pyryrolyl)acrolein (25b, R' = H)

A solution of 3-(N,N-dimethylamino)acrolein (16b, R' = H; 2.97 g, 30 mmol) and N-methylpyrrole (24b; 5 ml, 33.8 mmol) in chloroform (10 ml) is added dropwisely to phosphorous chloride (2.75 ml, 30 mmol) dissolved in chloroform (5 ml) at -10 °C. After stirring for 1 h at this temperature, an aqueous solution of sodium perchlorate (30%, 20 ml) is added rapidly. The resulting precipitate is filtered by suction, dried, and stirred thoroughly for 2 h with aqueous potassium hydroxide (5 normal, 10 ml) and chloroform (30 ml). After filtration, the organic layer is separated, dried, and concentrated in vacuo. The residue is recrystallized from chloroform/petroleum ether (40:60); yield: 2.2 g (49.3%); m.p. 99°C.

4. Cyclization of 3-Alkoxyacroleins with Heterocyclic Enamines

4.1. Azopyridazines

1H-Pyrazolo[3,4-b], isoxazolo[5,4-b], and isothiazolo [3,4-b]pyridines are obtained by the reaction of 1 with

\[ \text{C}_2\text{H}_5\text{O} + \text{RCHO} + \text{H}_3\text{N} - \text{N} - \text{R}^2 \rightarrow \text{R}^2 - \text{C}_2\text{H}_5\text{OH} \]

26, 27a, b, 28

5. Cyclizations of 3-Ethoxyacroleins with Amides and Related Compounds

5.1. 2,5-Disubstituted Pyrimidines

2,5-Dialkylpyrimidines arise from cyclocondensation of 3-ethoxyacroleins 1 and amidinium chlorides 36. Yields are much better than those achieved with the corresponding malonic dialdehyde tetraacetals 8.

\[ \text{OS} + \text{NH}_2\text{R} + \text{H}_2\text{N} - \text{R}^2 \rightarrow \text{C}_2\text{H}_5\text{OH} \]

36

Hydroxy-, thiol-, and amino functions X at position 2 of the pyrimidine ring can be introduced when the cyclocondensation of 1 is performed with urea (38a), thiourea (38b), and guanidine (38c), respectively.
5.2. Azolopyrimidines with Bridgehead Nitrogen

Heterocyclic amidines such as 5-amino-1H-pyrazol (40), 3-amino-1,2,4-triazole (41), 5-aminopteridin 42 26 cyclocondense with 3-ethyacyroleins 1 or their precursors 8 to pyrazolo[1,5-α]pyrimidines 43, 24 triazolo[1,5-α]pyrimidines 44, 25 and tetrazolo[1,5-α]pyrimidines 45, 26

A 3-hydroxypropyl side chain is introduced at position 6 by 3,4-dihydro-2H-pyran-5-carbaldehyde (2) or its precursor 15 as heterocyclic 3-alkoxyacrolein

6-(3-Hydoxypropyl)-1,2,4-triazolo[1,5-α]pyrimidine (44b):
3-Amino-1H-1,2,4,3-triazole (41) g, 30 mmol) is refluxed with 2-ethoxytetrahydroquanyl-3-carbaldehyde diethyl acetal (15, 8.36 g, 30 mmol) in glacial acetic acid (50 ml). After evaporation of acetic acid under reduced pressure, the residue is recrystallized from toluene/ethanol and dried over diphosphorous pentoxide at 0.27 mbar: yield: 2.5 g (47%); m.p. 95 °C.

Tetrazolo[1,5-α]pyrimidines 45 have been shown by 1H-NMR to equilibrate with 2-azidopyrimidines 46, 26 which may undergo 1,3-dipolar cycloadditions as characteristic of azides. 22

6. Cyclizations with Hydrazines

6.1. Pyrazoles

3-Ethyacyroleins 1 and their precursors 8 cyclocondense with hydrazines 51 to yield pyrazoles 52.

This modification of a well known ring closure 29 takes preference when the formation of six- or seven-membered rings is also possible due to the presence of amidino- or enyhdrazino functions. Thus, aminoguanidine 53 does not yield 2-hydrazinopyrimidines 54 when reacted with 3-ethyacyroleins 1.

Instead, N-aminopyrazoles 55 can be isolated as hydrochlorides. 23

In keeping with the preference for pyrazole formation, 6-hydrazinouracil 56a and 3-ethyacyroleins 1 cyclocondense to give 6-(1-pyrazolyl)-pyrimidines 57. 1H-Pyrimido[4,5-c]diazepines 58 are not isolated. 30

6.2. 1H-Pyrimido[4,5-c][1,2]diazepines

If the nitrogen of 6-hydrazinouracils is methylated (e.g. 56b), annelation with 3-ethyacyroleins 1 occurs at the nucleophilic pyrimidine carbon C-5. 1H-Pyrimido[4,5-c][1,2]diazepines 58 are isolated in reasonable yields. 30
7. Cyclizations with Enediamines

7.1. Diazepines

1,2-Diaminobenzenes (e.g. 59) and 1,3-diketones or their enols (e.g. 60) react in acidic solution to yield violet 2,5-dialkyl-1,5-benzodiazepinium chlorides (e.g. 61) as primary products. The yellow diazepine tautomers 62 can be isolated upon neutralization with sodium hydroxide.

The formation of diazepines from 3-ethoxyacrolics 1, as 1,3-dialdehyde equivalents, and 1,2-diamino substituted aromatic rings such as 59 appears to be the exception. Examples are pyrrolo[3,4-b][1,4]diazepines 64, obtained in poor yields from 3,4-diamino-N-methylpyrrole 63 and 3-ethoxyacrolics 1.2

7.2. Dihydro-1,4,8,11-tetraaza[14]annulenes

2,5-Dialkyl-1,5-benzodiazepinium salts 61 have been shown to be converted into the metal chelates 66 of 5,7,12,14-tetraalkyl-1,8-dihydro-1,4,8,11-tetraaza[14]annulenes in the presence of nickel(II) salts. This bimolecular ring expansion follows the pattern of a metal template reaction: the intermediate 65 is a metal chelate in which two substrate molecules 62 are coordinated by the metal ion; this arrangement efficiently prepares both substrate molecules for an expansion to the macrocycle 66.

1,8-Dihydro-1,4,8,11-tetraaza[14]annulenes 69 are directly formed from enediamines such as dianimomaleodinitrile 67 and 3-ethoxyacrolics 1.44 Yields of the macrocycles 69 are substantially improved by an application of the metal template effect. A metal cation is used which coordinates the enediamine 67 in the complex 68 prior to the cyclocondensation, but which does not fit into the cavity of the target macrocycle 69 because its ionic radius is too large or too small (r ≫ 70 pm). As a result, the template ion is readily lost upon formation of the ring 69, whereby the yield still benefits from the metal template effect. The best results are achieved with chromium(III) salts. Nickel(II) chelates 70 (M = Ni) are obtained with nickel(II) acetate as template salt; the nickel(II) ions (r_{ Ni^{II} } = 70 pm) exactly fit into the cavity of the ligand 69.
product is filtered by suction from the cooled reaction mixture, washed with methanol and dried. Extraction with toluene in the Soxhlet extractor affords blue needles crystallizing from the deep green hot extract. Upon cooling, the crystals are filtered by suction, washed with methanol, and dried in vacuo; yield: 4.9 g (61%); m.p. 178 C.

In similar procedures, 1,8-dihydrodibenzo[4,5]1,4,8,11-tetraaza[14]annulences 72 are obtained from 1,2-diaminobenzene, as well as from its substituted derivatives 71 and 3-ethoxyacroleins 1. Reaction of the N₄ macrocycles 72 with nickel(II) salts affords the nickel(II) chelates 73, which can also be directly prepared by nickel(II)-template reaction of the diamines 71 with 3-ethoxyacroleins 1.

Hydroxypropyl groups (R = CH₂CH₂CH₂OH) can be introduced at the centers of both C₃ bridges of the macrocycles 72 when 3,4-dihydro-2H-pyran-5-carbaldehyde 2 is applied as heterocyclic 3-alkoxyacrolein. The introduced functions permit further derivatizations of the macrocycles 74 and the introduction of additional chelate ligands.

Several other aromatic 1,2-diamines have been cyclocondensed with 3-ethoxyacroleins 1, whereby 1,8-dihydro-1,4,8,11-tetraaza[14]annulences 76–79 with two fused benzocrown[5] rings, as well as with five-membered heterocycles such as thiophene, thiadiazole, and oxadiazole, could be prepared in this manner.

8. Reductive Coupling of 3-Ethoxyacroleins (McMurry Reaction)

McMurry reductive coupling of carbonyl compounds has been applied to the synthesis of sterically crowded alkenes. 3-Ethoxyacroleins 1 also undergo McMurry type reductive coupling, but 2,5-dialkylhexa-2,4-diendials 84 are the products. The mechanism probably follows the pattern proposed for carbonyl compounds, involving an intermediate pinacol-titanium complex at the surface of the active titanium specie and acid catalyzed elimination of ethanol. E-Configuration at the 2,3-4,5-double bonds of the dialdehyde 84 can be derived from three-bond carbon-13-proton couplings in the ¹³C-NMR spectra.

2 C₂H₄O₂ + H₂ → 84

(E,E)-2,5-Dimethyl-2,4-hexadienedial (84, R¹ = CH₃) is added to titanium(III)chloride (3.1 g, 20 mmol) placed in a Schlerk reactor under nitrogen. The...
mixture is cooled to 0°C, and lithium aluminium hydride (0.38 g, 10 mmol) is added slowly so that evolution of hydrogen remains under control. The color of the mixture changes from violet to black upon complete addition of the reducing reagent. The mixture is stirred for 30 min at 0°C, refluxed for 1 h in order to prevent hydrogenations, and finally cooled to 0°C.

A solution of 2-methyl-3-ethoxyacrolein (1, R¹ = CH₃; 2.28 g, 20 mmol) dissolved in anhydrous tetrahydrofuran (10 ml) is added dropwise to the McMurry reagent, freshly prepared as described above, at 0°C under nitrogen in the Schlenk reactor. After completion of the addition, the mixture is allowed to reach room temperature, is stirred for one hour and is again cooled to 0°C. Aqueous hydrogen chloride (2 normal, 40 ml) is added carefully. The resulting solution is extracted with chloroform (5 x 40 ml); the chloroform extract is washed with water (3 x 40 ml) and dried with magnesium sulfate. Evaporation of the filtrate under reduced pressure yields a yellow oil, which is purified by column chromatography (silica gel, chloroform/methanol, 100:0.75). Evaporation of the main fraction affords a yellow solid, which is recrystallized from ethanol to give yellow crystals; yield: 0.81 g (29.3%); m.p. 156°C.

9. Reactions with Carbon Nucleophiles

9.1. C-C Connections with Enamines

Lewis acid catalyzed addition of 3-ethoxyacroleins 1 to the nucleophilic carbon of enamines 85 involves the aldehyde function, and 2-(3'-ethoxy-1'-hydroxy-2'-propenyl)cycloalkanes 87 are obtained upon slightly acidic hydrolysis of the zwitterionic intermediate 86.

(5)-2-Methyl-3-(3-pyridyl)acrolein (92, R¹ = CH₃, R² = 3-Pyridyl) 44-47 Bromoethane (1.5 g, 10 mmol) is added dropwise slowly to ether (20 ml) containing sodium cyanide (5.8 g, 20 mmol). When the mixture of the reaction has subsided, a mixture of bromoethane (15 g, 140 mmol), 3-bromopyridine (8.0 g, 50 mmol), and ether (20 ml) is added dropwise at such a rate that the solution boils smoothly. After refluxing for 0.5 h a yellow precipitate has formed; the ether is distilled off slowly, with heating, until the residue becomes a brown viscous liquid. This residue is diluted slowly with tetrahydrofuran (40 ml). The resulting solution is refluxed for 1 h and cooled in an ice bath. 3-Ethoxy-2-methylacrolein (1, R¹ = CH₃; 28 g, 200 mmol) in ether (100 ml) is then added dropwise. The mixture is stirred for 2 h at room temperature and hydrolyzed in an ice bath with 2 normal aqueous sulfuric acid (200 ml). The ether phase is separated and washed with 2 normal aqueous sulfuric acid (2 x 20 ml). Concentrated aqueous ammonia is added to the ice cooled combined sulfuric acid solution until it becomes basic. The alkaline solution is extracted with ether (3 x 50 ml). Evaporation of solvent affords a yellow oil, which crystallizes in the refrigerator. Colorless needles are obtained upon recrystallization from hexane; yield: 4.1 g (56%); m.p. 45°C.

9.2. Oxopropenylolation of Alkylmagnesium Halides

Electrophilicity of the aldehyde carbon obviously predominates when 3-ethoxyacroleins 1 are reacted with carbon nucleophiles. But subsequent hydrolysis of the γ-hydroxyenol ethers similar to 87 may give rise to the formation of α,β-unsaturated aldehydes so that oxopropenylations of carbon nucleophiles

9.3. Oxopropenylolation of 1,3-Dithiane

Lithiated 1,3-dithiane 93 adds to 3-ethoxyacroleins 1 at -70°C to give [3-(1,3-dithian-2-yl)-3-hydroxy-1-propenyl] ethyl ethers 95 as primary products, probably involving the lithium chelates 94 as intermediates. 48 (E)-3-(1,3-Dithian-2-yl)acroleins 96 are obtained in good overall yields upon acidic hydrolysis of the enol ethers 95. 48 The E configuration is detectable by NMR. 48 Fumaryl didehyde 97 can be liberated when necessary from the dithianylacroleins 96 by oxidative cleavage with N-bromosuccinimide in acetonitrile. 48

9.4. Cycloamination of Metallated 2-Picoline to Quinolizinum Salts

Lithiated 2-picoline 98 reacts with 3-ethoxyacroleins 1 primarily according to the reaction patterns described above, yielding [4-(2-pyridyl)-3-hydroxy-1-butenyl] ethyl ethers 99, which can be isolated, but are readily converted into the 3-alkylquinolininium salts 100 upon addition of acids. 49
are achieved when the ylide 103 is generated in situ from its phosphonium salt precursor with lithium disopropylamide as base.51

Correspondingly, 3,4-dihydro-2H-pyran-5-carbaldehyde 2, as heteroaryl cyclic 3-alkoxyacrolein, yields 5-vinyl-3,4-dihydro-2H-pyran when reacted with the ylide 103.32

2-n-Pentyl-1-ethoxy-1,3-butenadiene (104, R1 = n-C4H9): Disopropylamine (9.8 ml, 70 mmol) in anhydrous tetrahydrofuran (120 ml) is cooled to −78 °C. n-Butyllithium (15% solution in hexane, 43.7 ml, 70 mmol) is added dropwise under nitrogen during a period of 10 min. After the solution is allowed to warm to 0°C and is kept at this temperature for 30 min, methylenetriphenylphosphorane bromide (21.4 g, 60 mmol) is added to the solution with stirring. Stirring is continued at room temperature for 1 h. 2-Pentyl-3-thoxoacrolein (R1 = n-C4H9, 8.5 g, 50 mmol) is added dropwise to the pale yellow solution, which changes color to orange. The mixture is stirred at room temperature for 1 h and poured into crushed ice (200 g). The resulting solution is extracted with petroleum ether (40–60 °C) 3 times. The combined extracts are dried with sodium sulfate, filtered by suction, and evaporated in vacuo. Additional triphenylphosphinoxide crystallizes overnight from the oily residue in the refrigerator and is filtered off by suction. Distillation of the filtrate under reduced pressure affords 104, R1 = n-C4H9; yield: 5.8 g (69%); b. p. 88 °C/21 mbar; stable when kept in the refrigerator.

Wittig alkenylation of 3-ethoxyacroleins 1 and 3-(N,N-dimethylamino)-acroleins 162 is a general procedure for the preparation of various donor substituted 1,3-diens. These are useful for [4 + 2] cycloadditions with less reactive dienophiles such as nitriles, resulting in a pyridine synthesis,23 and carbonyl compounds. [4 + 2] Cycloadditions of diethyl mesoxalate to 1-ethoxy-1,3-butadienes 104, for example, efficiently yield the enantiomers of 3-alkyl-2-ethoxy-6,5-diehdroxy-carbonyl-5,6-dihydro-2H-pyran 105.54 The potential of this hetero Diels-Alder reaction for the synthesis of carbohydrate derivatives has already been recognized.

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9.5. γ-Alkylpentameth cycyanine Perchlorates from 3-Ethoxyacroleins

3-Ethoxyacroleins 1 behave as bifunctional C1 electrophiles when reacted with heterocyclic a-carbon nucleophiles, such as Fischer base 101, 2-methyl-N-alkylthiazolium salts, or 2-methyl-N-alkylquinolinium salts. Cyanine dyes such as γ-alkylpentamethcycyanine perchlorates, e. g. 102, are isolated.50

10. Reactions with Ylides

2-Alkyl-1-ethoxy-1,3-butenadienes 104 are conveniently obtained by Wittig alkenylation of 2-alkyl-3-ethoxyacroleins 1, e. g. with triphenylphosphine methyldide 103. So far, the best yields

Supplemental References

Synthesis of 3-Ethoxycroleanes and Precursors


Synthetic Application of 3-Ethoxycraneanenes and Related Compounds


(64) Schmidt, R. R., Karg, J., Guillaud, W. Chem. Ber. 1977, 110, 2433 (Glycosylhydrazines from 1,3-Dicarbonyl Compounds).


Vinanimides and Vinaminidinum Salts as Aza Analogs of 3-Ethoxycroleanes


Vinlogs of 3-Ethoxy- and 3-Aminoethoxycroleanes