0.5 hr, the mixture was cooled to 25° C and filtered. The solid was washed with methanol and dried to obtain 0.7 gram (99%) of 6e, mp 201–204° C. Recrystallization from toluene gave the analytical sample, mp 202–204° C.

3-Phenoxy-$\Delta^{1,1'}$-indenemalononitrile (7a). Derivative 5 (0.5 gram) was added to a mixture of sodium hydroxide (0.5 gram) and phenol (6 grams) at 75° C. The resulting mixture was heated to 95° C, stirred for 15 min, and then poured into 5% aqueous sodium hydroxide solution (75 ml). Filtration removed 0.45 gram (71%) of crude 7a mp 160° C. Recrystallization from toluene/hexane gave the analytical sample, mp 164–165° C.

3-Methoxy-$\Delta^{1,1'}$-indenemalononitrile (7c). A solution of sodium methoxide (0.3 gram) in methanol (50 ml) was refluxed during the addition of 5 (0.5 gram). After the solution had refluxed for 5 min, water (75 ml) was added, and the precipitate was removed by filtration. The product (0.25 gram, 51%) melted at 153–156° C. Recrystallization from toluene/hexane gave the analytical sample, mp 162–164°.

3-Amino-$\Delta^{1,1'}$-indenemalononitrile (7d). Anhydrous ammonia was added beneath the surface of a solution of 5 (1.0 gram) in methanol (30 ml) or toluene (30 ml) until 5 was no longer detectable by thin-layer chromatography (20 min). Filtration afforded 0.5 gram (55%) of solid, mp > 300° C. The solid was refluxed with ethanol (15 ml) and filtered hot to give the analytical sample, mp > 300° C.

3-Piperidino-$\Delta^{1,1'}$-indenemalononitrile (7f). Derivative 5 (0.5 gram) was added portionwise to piperidine (10 ml) while the reaction mixture was cooled in an ice bath (exothermic reaction). The mixture was stirred for 5 min at 25° C and then diluted with water (100 ml). Filtration gave 0.6 gram (97%) of 7f, mp 169–173° C. Recrystallization from toluene gave the analytical sample, mp 174–175° C.

2-[*p*-(Dimethylamino)benzylidene] [$\Delta^{1,2'}$-biindan]-1′,3,3′-trione (8a). A mixture of 2 (0.55 gram, 0.002 mole), *p*-(dimethylamino)benzaldehyde (0.37 gram), and acetic anhydride (10 ml) was stirred at 98° C for 2 hr and then cooled to 25° C. Filtration afforded 0.3 gram (37%) of crystals, mp 239° C. Recrystallization from chlorobenzene gave the analytical sample, mp 239° C.

2-[*p*-(Dimethylamino)benzylidene]-3-oxo-$\Delta^{1,1'}$-indanmalononitrile (9a). A mixture of 3 (0.39 gram, 0.002 mole), *p*-(dimethylamino)benzaldehyde (0.37 gram, 0.0025 mole), and acetic anhydride (10 ml) was stirred at 98° C for 2.0 hr and then cooled to 5° C. Filtration after 1 hr afforded 0.4 gram (62%) of crystals, mp 235–237° C. Recrystallization from chlorobenzene/hexane gave the analytical sample, mp 238° C.

3-[*p*-(Diethylamino)phenyl]-$\Delta^{1,1'}$-indenemalononitrile (11a). A mixture of 5 (0.49 gram, 0.0025 mole), *N,N*-diethylaniline (0.45 gram, 0.003 mole), chlorobenzene (5 ml), and phosphoryl chloride (3 ml) was stirred at 105° C for 1 hr. An additional 6 ml of *N,N*-diethylaniline was then added, and stirring was continued at 120° C for 2 hr. The reaction mixture was then poured into a 100/50/50 mixture of ice/5% hydrochloric acid/hexane. The gummy precipitate was collected by filtration and recrystallized from isopropyl alcohol/hexane. Derivative 11a (0.25 gram, 31%) was obtained, mp 138–165° C. Recrystallization from toluene/hexane gave the analytical sample; needles, mp 141–170° C.

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Alkylation of 5-Membered Ring Acyloins and 1,2-Diketones

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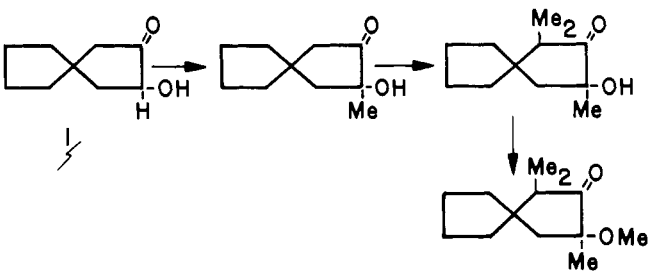
The order of alkylation of 5-membered acyloins in basic solution is first on carbon which carries the hydroxyl function, then on carbon alpha to the carbonyl, and finally alkylation on the alcohol. The order of alkylation of 1,2-diketones in basic solution is first on oxygen of the enol and then on carbon alpha to the ketone.

The two major acyloin condensation review articles (*4*, *8*) emphasize synthetic utility, with no mention of the reactions of acyloins. Monoalkylation of acyloins has been studied (*11*, *12*). We have found that the alkylation of 5-membered ring acyloins under basic conditions (sodium hydride–glyme) using methyl iodide, takes place in the following order:



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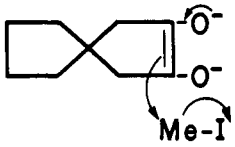
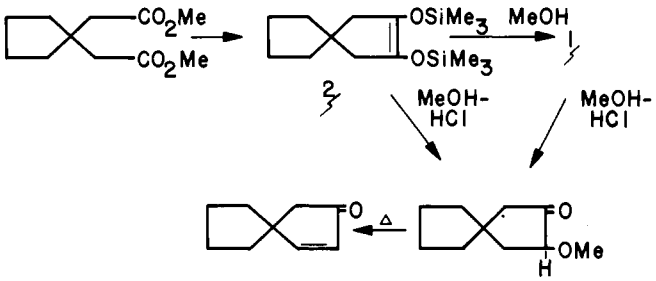
An explanation (9) for the first alkylation lies in the fact that the acyloin in base forms the dianion of the enediol, which acts as a nucleophile in the matter shown. In subsequent reactions, C-alkylation alpha to the carbonyl is favored over O-alkylation.

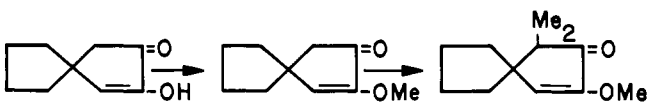


The starting acyloin 1 was prepared via the following reaction sequence using trimethylchlorosilane (*1*, *2*, *10*):



Under acidic conditions, the O-methyl compound was formed in good yield. This is similar to the report (*5*) that benzoin and methanolic hydrogen chloride gave the O-methyl product. This compound was readily thermolyzed to the α,β-unsaturated system as shown above.

Alkylation of 1,2-diketones has not been studied systematically. When we used a 5-membered ring 1,2-diketone (100% enol in this system), and employed sodium hydride–glyme and methyl iodide, the following order of alkylation was found. O-alkylation is reported (*3*), but C-alkylation



is not recorded. It was not possible to isolate the mono-C-alkylated product by our procedure.

The alkylation of other aliphatic acyloins and 1,2-diketones would appear to behave similarly.

EXPERIMENTAL

Dimethyl Cyclopentane-1,1-diacetate. This ester was prepared from cyclopentane-1,1-diacetic acid (*7*) using methanol and sulfuric acid in the usual manner. The compound boiled at 100° at 0.75 mm.

2,3-Bis(trimethylsilyloxy)spiro[4,4]non-2-ene (2). About 100 ml of dry toluene was distilled into a 250-ml round-bottom three-neck flask equipped with mechanical stirrer, dropping funnel, and water condenser. Sodium dispersion (2.8 grams, 0.12 g-atom) was prepared under a helium atmosphere. The mixture was cooled, and 10 ml of trimethylchlorosilane was added. The mixture was heated to reflux again and 5.3 grams (0.025 mole) of dimethyl cyclopentane-1,1-diacetate in 50 ml of toluene was added dropwise over a period of 2 hr followed by heating under reflux for an additional 8 hr. The mixture was cooled, filtered, and the filtrate was concentrated. The residue was distilled and gave 6.5 grams (87% yield) of compound 2, bp 95° at 0.25 mm; nmr (CCl_4) τ 7.8 (4 H) 8.4 (broad, 8 H) and 9.85 (18 H); ir (liquid film), an unusual triplet absorption at 1750 (w), 1700 (s) and 1650 (w) cm^{-1}.

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

Solvolysis of Compound 2. (a) A solution of 3 grams of compound 2 and 50 ml of absolute methanol was refluxed under a nitrogen atmosphere for 2 hr. After removal of the methanol, the residue was distilled under reduced pressure to give 3-hydroxy-spiro[4,4]nonan-2-one (1) in 85% yield, bp 95° at 0.25 mm; nmr ($CDCl_3$) τ 5.8 (triplet, 1 H), 6.5 (broad, 1 H, D_2O exchanged), 7.75 (1 H), 7.80 (1 H) and 8.3 (broad, 10 H); ir (liquid film) 3500 and 1725 cm^{-1}.

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

Compound 2, on standing, formed a dimer, mp 101–104°; nmr ($CDCl_3$) τ 6.0 (triplet, 2 H), 7.1 (2 H, D_2O exchanged), 8.1 (4 H) and 8.4 (20 H); ir bands at 3500 and 2900 cm^{-1}, but no carbonyl band was present.

(b) The above reaction was repeated using methanol saturated with hydrogen chloride. Distillation gave an 83% yield of 3-methoxy-spiro[4,4]nonan-2-one, bp 70° at 0.25 mm; nmr (CCl_4) τ 6.5 (multiplet, 4 H), 7.8 (multiplet, 2 H) and 8.3 (broad, 10 H); ir bands at 2950, 1740, and 1710 cm^{-1}.

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

A sample of compound 1, dissolved in methanol saturated with hydrogen chloride, was heated under reflux for 0.5 hr. Distillation under reduced pressure gave 3-methoxy-spiro[4,4]nonan-2-one.

A 1.8-gram sample of 3-methoxy-spiro[4,4]nonan-2-one was heated at 100° at atmospheric pressure for 2 hr. A distillation under reduced pressure gave 1 gram (73% yield) of spiro[4,4]non-1-ene-3-one, bp 45° at 0.25 mm; nmr (CCl_4) τ 2.6 (doublet, 1 H), 4.1 (doublet, 1 H), 7.9 (2 H) and 8.4 (broad, 8 H); ir bands at 2940, 2860, 1700, and 1580 cm^{-1}.

Alkylation of Compound 1. (a) A solution of 3.1 grams (0.02 mole) of compound 1 and 20 ml of glyme was added slowly to 0.72 gram (0.016 mole) of 57% of sodium hydride and 10 ml of glyme. The mixture was stirred at room temperature for 0.5 hr and 2.8 grams (0.02 mole) of methyl iodide was added and stirring was continued for 0.5 hr. The mixture was cooled, filtered, and concentrated. The residue was treated with 20 ml of saturated salt solution and was extracted twice with 50 ml portions of ether. The ether extract was dried and distilled to give 1.9 grams (70% yield) of 3-hydroxy-3-methyl-spiro[4,4]nonan-2-one, bp 78° at 0.5 mm; nmr (CCl_4) τ 6.7 (1 H, D_2O exchanged), 7.7 (2 H), 8.0 (2 H), 8.4 (8 H), and 8.7 (3 H); ir (KBr pellet) 3500, 2950, 2930, and 1750 cm^{-1}.

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

(b) A solution of 1.5 grams (0.01 mole) of compound 1 and 10 ml of glyme was added slowly to 0.9 gram (0.02 mole) of 57% sodium hydride and 10 ml of glyme. The mixture was stirred at room temperature for 0.5 hr; 2.8 grams (0.02 mole) of methyl iodide was added and stirring was continued for 0.5 hr. After removal of the glyme, the residue was distilled under reduced pressure to give 1 gram (50% yield) of 3-hydroxy-1,1,3-trimethyl-spiro[4,4]nonan-2-one, bp 90° at 0.5 mm; mp 67°; nmr ($CDCl_3$) τ 7.5 (1 H, D_2O exchanged), 7.95 (1 H), 8.05 (1 H), 8.4 (8 H), 8.7 (3 H), and 9.0 (6 H).

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

(c) A solution of 3 grams (0.02 mole) of compound 1 and 20 ml of glyme was added to 4.5 grams (0.1 mole) of 57% sodium hydride, and stirring was continued for 0.5 hr. Methyl iodide (21 grams, 0.15 mole) was added slowly with cooling. After it was stirred for 0.5 hr at room

temperature, the mixture was filtered and the filtrate was distilled to give 2.8 grams (67% yield) of 3-methoxy-1,1,3-trimethyl-spiro[4,4]nonan-2-one, bp 80° at 0.5 mm; nmr (CCl_4) τ 6.8 (3 H), 7.95 (1 H), 8.10 (1 H), 8.4 (8 H), 8.8 (3 H), 8.95 (3 H) and 9.05 (3 H); ir bands at 2950 and 1725 cm^{-1}.

Elemental analyses (C and H), in agreement with the theoretical values have been obtained and submitted for review.

Alkylation of 2-Hydroxy-spiro[4,4]non-1-ene-3-one. (a) A solution of 1.5 grams (0.01 mole) of 2-hydroxy-spiro[4,4]non-1-ene-3-one (*6*) and 20 ml of glyme was added slowly to a stirred suspension of 10 ml of glyme and 0.42 gram (0.01 mole) of 57% sodium hydride. After stirring for 1 hr, 1.4 grams (0.01 mole) of methyl iodide was added and, after an additional 0.5-hr stirring period, the mixture was poured into 20 ml of 3*N* hydrochloric acid and worked up in the usual manner. Distillation of the residue gave 1.8 grams (88% yield) of 2-methoxy-spiro[4,4]non-1-ene-3-one, bp 120° at 0.25 mm; nmr (CCl_4) τ 3.85 (1 H), 6.3 (3 H), 7.8 (2 H) and 8.3 (broad, 8 H).

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review. (b) A solution of 1.5 grams (0.01 mole) of 2-hydroxy-spiro[4,4]non-1-ene-3-one (*3*) and 20 ml of glyme was added slowly to a stirred suspension of 10 ml of glyme and 1.68 grams (0.04 mole) of 57% sodium hydride. The mixture was stirred for 1 hr and 5.2 grams (0.04 mole) of methyl iodide was then added slowly. After it was stirred for 2 hr, the mixture was poured into 30 ml of 3*N* hydrochloric acid and was worked up in the usual way. The residue was distilled to give 1 gram (60% yield) of 4,4-dimethyl-2-methoxy-spiro[4,4]non-1-ene-3-one, bp 100–102° at 0.25 mm. It solidified and was recrystallized from Skellysolve B, mp 59°; nmr (CCl_4) τ 3.85 (1 H), 6.3 (3 H), 8.2 (broad, 8 H) and 9.0 (6 H); ir bands at 2950, 1750, and 1620 cm^{-1}.

Elemental analyses (C and H) in agreement with the theoretical values have been obtained and submitted for review.

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N,N-Dialkyl Carbamates of Diols

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The condensation of *N,N*-diethyl and *N,N*-dimethyl carbamyl chloride with alcohols is readily accomplished by reaction of the sodium alkoxide with the dialkyl carbamyl chloride. The physical constants are given for 26 new dialkyl carbamates which were tested for activity against Sarcoma 180.

Carbamates have been prepared from carbamyl chlorides and alcohols in the presence of pyridine (*1–4*, *6*) or potassium hydroxide (*7*), but neither of these techniques was satisfactory for the diols under study. Conversion of these diols to their sodium salts by treatment with sodium hydride in dry dioxane and reaction of this salt with the carbamyl chloride proved to be a satisfactory procedure, and the 26 new *N,N*-diethyl and *N,N*-dimethylcarbamates listed in Table I were prepared by this technique.

A typical preparation was performed as follows: Six grams (0.051 mole) of 3-methylpentane-1,5-diol in 50 ml of anhydrous dioxane was added dropwise to a nitrogen-swept stirred suspension of 6.54 grams (0.14 mole) of 53% oil-dispersed sodium hydride in 50 ml of dry dioxane. This mixture was refluxed for 6 hours. Then 15.05 grams (0.14 mole) of dimethyl carbamyl chloride was added dropwise with stirring. This produced a vigorous reaction, so the addition was made slowly, about 1 to 2 hours, while reflux was maintained. After addition of the carbamyl chloride, reflux was continued for 15 hours. The reaction mixture was allowed to cool to room temperature and filtered. The filtrate was stripped of dioxane and the crude product distilled to give 8.2 grams (63% theoretical) of colorless liquid, boiling at 120°/0.15 mm, n_D^{28} = 1.4555. The physical data for this compound, 3-methyl-1,5-pentamethylene-bis(*N,N*-dimethyl carbamate), are given in Table II.

In general, the yields of biscarbamate are only fair, apparently because the reaction is complicated by formation of considerable amounts of monocarbamate, which often makes the separation of products difficult. The infrared spectra given in Table II are generally consistent with the carbonyl absorption frequency of 1687 ± 4 cm^{-1} observed previously (*5*) for such compounds. However, there are exceptions caused by effects of the structure of the compounds. Also, in some cases, shoulders or doubling of the carbonyl peaks are observed, but these are often obscured by the overlap produced by the two carbonyl groups of the molecule.

3-Methyl-2-pentene-1,5-diol was synthesized by the lithium aluminum hydride reduction of *cis-trans*-ethylmethyl-β-methylglutaconate in 51% yield; bp 98/0.2 mm; n_D^{25} = 1.4785.

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