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SYNTHESIS OF TRICYCLIC KETONES BY COPPER-CATALYZED CYCLIZATION OF MONOCYCLIC OLEFINIC DIAZOKETONES

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Abstract—Intramolecular trapping of intermediates of the copper–ketocarbene type by the double bond of monocyclic olefins leads to a variety of tricyclic ketones. The photolytically generated ketocarbene cannot be trapped in this way to a significant degree. Sufficient examples of the method are given to indicate its general usefulness in the synthesis of ketocyclopropanes.

DIAZOKETONES decompose in the presence of copper to a type of intermediate which has been found to react with olefins to produce derivatives of ketocyclopropane. The pioneering examples of Šorm *et al.* are intermolecular,[2] while a recent illustration provided by Stork and Ficini[3] is an intramolecular cyclization of 1-diazohept-6-en-2-one to bicyclo[4. 1. 0]heptan-2-one. In this research, the reaction has been extended to the synthesis of tricyclic ketones.[4] Some of these compounds are relevant to the proof of structure of molecules encountered in a synthesis of bullvalene; others are of interest for their strained nature.[5] The general outline of the syntheses is illustrated below along with a list of the specific molecules to which it has been applied.

Tricyclo[5.2.1.$0^{2,10}$]*deca-9-one* (I; *tetrahydro-isobullvalone*)

The starting material for the synthesis of this material, 2-cyclohepten-1-ylacetyl chloride, is prepared by the sequence of Mennrath and Gauducheau[6,7] from cycloheptene by bromination to 3-bromocycloheptene,[8,9] conversion to diethyl 2-cyclohepten-1-ylmalonate, saponification, decarboxylation, and treatment with thionyl chloride. Reaction of the acid chloride with excess of diazomethane affords the diazoketone which is converted to the tricyclic ketone (I) in 36% of theory (based on the acid chloride) by being heated in boiling hexane with anhydrous cupric sulfate.

[1] We wish to express our deep gratitude to the Undergraduate Research Participation Program of the National Science Foundation for its support of this work through the award of Summer Research Fellowships and Research Assistantships and through research grants 11378 and 0959.

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[4] The first example of this application, the synthesis of tricyclo[3.3.1.$0^{4,6}$]octa-2,7-dien-9-one by B. Ferrier, has been reported briefly [W. Doering, *Zh. Vsesoyuz. Khim. Obsh. Mendeleeva* **7**, 308 (1962)].

[5] For the synthesis by this method of a very highly strained molecule, 2,4-dimethyl-tricyclo[1.1.1.$0^{2,4}$]-pentan-5-one, see W. von E. Doering and M. Pomerantz, *Tetrahedron Letters* 961 (1964).

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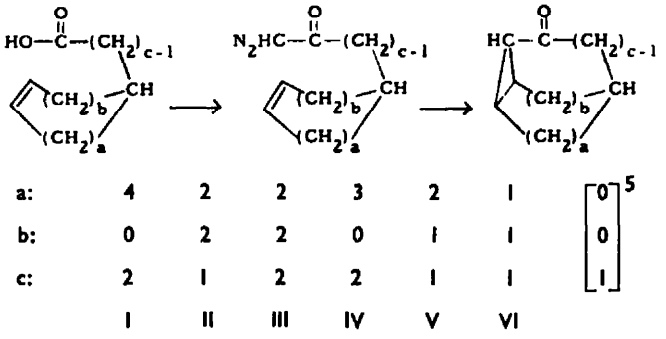

	I	II	III	IV	V	VI	
a:	4	2	2	3	2	1	[0]5
b:	0	2	2	0	1	1	0
c:	2	1	2	2	1	1	1

Tricyclo[3.3.1.$0^{2,8}$]*nonan-9-one* (II; *tetrahydrobarbaralone*)

4-Cyclohepten-1-carboxylic acid, the starting material for the synthesis of II, is prepared from cyclopentanone by the elegant four-step sequence devised by Stork *et al.*[10,11] The diazoketone, which is obtained from the corresponding acid chloride in the usual way, is converted to the tricyclic ketone II by treatment with copper powder, anhydrous cupric sulfate or cuprous iodide.

Tricyclo[3.3.2.$0^{2,8}$]*deca*-3-*one* (III; *tetrahydrobullvalone*)

The starting material for the synthesis of III is 4-cyclohepten-1-ylacetic acid, which may be obtained through the Wolff rearrangement of diazomethyl-4-cyclohepten-1-ylketone, the intermediate in the synthesis of II. It is worth noting that this Arndt-Eistert synthesis procedes normally with silver oxide as catalyst without appreciable interference from addition to the double bond.[12] Were it not for the report of Yates and Fugger[13] that cuprous iodide in methanol–acetonitrile catalyzes the Wolff rearrangement of diazoacetophenone, the copper catalysts would be uniformly distinguished from silver and platinum in their effect on diazoketones. As mentioned already, in the present instance of 4-cyclohepten-1-yldiazomethylketone, cuprous iodide does not behave differently from other copper catalysts: it catalyzes the intramolecular cyclization to II without appreciable interference from the Wolff rearrangement.

III may also be obtained from II by the conventional ring enlargement of cyclic ketones with diazomethane. This reaction leads to a pair of ketones, of which the major one is identical in all respects to III and of which the minor one is presumed to be the isomeric tricyclo[3.3.2.$0^{2,8}$]decan-4-one.

Tricyclo[3.3.1.$0^{2,9}$]*nona*-3-*one* (IV)

The synthesis of this ketone follows that of the others. The starting acid, 2-cyclohexen-1-ylacetic acid, is prepared by the scheme outlined by van Tamelen and Shamma.[14]

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Tricyclo[2.2.2.0^{2,6}]*octan*-3-*one* (V)

Cyclization of 3-cyclohexen-1-yldiazomethylketone, prepared from cyclohexene-4-carboxylic acid[15,16] in the usual way, is effected by boiling in n-hexane with copper and leads to the formation of V in 31% of theory. A sample purified by g.l.p.c. is identical with the tricyclo[2.2.2.0^{2,6}]octan-3-one isolated by LeBel *et al.* from the oxidation of the major product of the solvolysis of derivatives of *exo*-bicyclo-[2.2.2]oct-5-en-2-ol.[17,18]

Tricyclo[2.2.1.0^{2,6}]*heptan*-3-*one* (VI; *nortricyclanone*)

3-Cyclopentene carboxylic acid has been prepared previously by Tiffeneau and Tchoubar[19] from the mono-epoxide of cyclohexadiene-1, 4 by rearrangement and oxidation[20] or disproportionation of the intermediate aldehyde.[20] It has also been prepared from *cis*-1, 4-dichloro and 1, 4-dibromobutene-2 with sodiomalonic ester.[21,22] In this work, the acid is prepared by carbonation of the Grignard reagent[22,23] derived from 4-bromocyclopentene.[24]

3-Cyclopenten-1-yldiazomethylketone, obtained in the usual way, is cyclized to nortricyclanone (VI) in 65% of theory by heating with copper powder in tetrahydrofuran under reflux. Establishment of identity rests on comparison with reported physical properties,[25,26] and more significantly, on direct comparison of the reduction product, tricyclo[2.2.1.0^{2,6}]heptan-3-ol, with a sample prepared by the method of Roberts *et al.*[25]

Photochemical decomposition of this diazoketone leads to a very complicated mixture of products which was not examined further. However, it is clear that intramolecular trapping of the free ketocarbene to produce nortricyclanone does not proceed to any significant extent.

EXPERIMENTAL

G.l.p.c. analyses and separations were carried out in Aerograph A-90 and A-90 P of the Wilkens Instrument and Research Co. IR spectra were determined in Perkin-Elmer Model 221 Spectrometer. NMR spectra were obtained on instruments A-60[27] and HR-60 of the Varian Associates Co.

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Tricyclo[5.2.1.$0^{2,10}$]*deca*-9-*one* (I). The preparation of 2-cyclohepten-1-ylacetic acid from cycloheptene follows that outlined without experimental detail by Mennrath and Gauducheau.[6] To a stirred, refluxing mixture of 52·5 g potassium t-butylate and 90·0 g diethylmalonate in 750 ml t-butyl alcohol, 80 g 3-bromocycloheptene (b.p. 67°/8 mm)[6-8] was added dropwise over a 1-hr period. After 5-hr further reflux, 600 ml t-butyl alcohol was removed by distillation. Addition of water, extraction with benzene and distillation afforded 43 g (38%) of product, b.p. 119–122°/2·0 mm. Saponification, effected by refluxing 24 hr in a mixture of 100 ml KOHaq and 100 ml EtOH, was followed by decarboxylation, effected by heating the crude malonic acid in 100 ml pyridine at 95° for 4 hr. Distillation at 105°/1 mm afforded 17 g 2-cyclohepten-1-ylacetic acid [reported b.p. 145°/15·3 mm;[6] b.p. 85°/0·2 mm[7]].

A solution of 14·5 g thionyl chloride and 17·0 g 2-cyclohepten-1-ylacetic acid in 250 ml ether was boiled under reflux for 5 hr. Distillation afforded 14·0 g acid chloride, b.p. 55–57°/1 mm; n_D^{25} 1·4915 (reported[6] b.p. 105°/16 mm). Reaction with ammonia afforded the corresponding amide, m.p. 128·5–129·5° (reported[6] m.p. 130°).

An ethereal solution of diazomethane (prepared from 27 g N-methyl-N-nitroso-urea, 200 ml 45% KOHaq and 350 ml ether at 0° and dried over KOH pellets) was treated with 14 g acid chloride. N_2 was evolved rapidly. After having stood overnight, the reaction was concentrated under red. press. to a yellow oil [δ = 5·23 ppm; ν_{max} 2100, 1640 cm^{-1}].

Without further purification, the diazoketone in 50 ml hexane was added to a boiling solution of 250 ml hexane containing 30 g anhydrous $CuSO_4$. After being stirred and boiled under reflux for 1 hr, the solution was filtered and concentrated. Distillation *in vacuo* afforded 4·0 g tricyclo[5.2.1.$0^{2,10}$]deca-9-one (I), b.p. 82°/1 mm. Chromatography on a 5-ft, Anakrom ABS, 50–60 mesh column at 150° (injector, 210°; detector, 270°) and He at 100 cc/mm showed the tricyclic ketone (ret. time 6–8 min) to be 93% of purity (n_D^{25} 1·5078).

An oxime, prepared in the usual manner, was recrystallized from MeOH; m.p. 106–108°. (Found: C, 72·6; H, 9·2. $C_{10}H_{15}NO$ requires C, 72·7; H, 9·2%).

Tricyclo[3.3.1.$0^{2,6}$]*nonan*-9-*one* (II). Cycloheptene-5-carboxylic acid was prepared by the method of Stork and Landesman.[11] In the final step, 26·5 g of the methiodide of 2-N-pyrrolidinylbicyclo-[3.2.1]octan-8-one was boiled under reflux in 150 ml 20% KOHaq for 3·5 hr. The reaction mixture was extracted with ether (discarded), acidified and extracted 4 times with 150-ml portions of ether. Extraction of the ethereal solution with Na_2CO_3aq, acidification, extraction with ether and concentration gave 8·3 g (65%) of cycloheptene-5-carboxylic acid, m.p. 64–66·5° (reported[11] m.p. 65–67°).

To a solution of 23·0 g of this acid in 200 ml benzene, 23·5 g thionyl chloride was added dropwise. After an immediate evolution of gas, the mixture was refluxed for 1·5 hr. Removal of benzene by distillation afforded an oil which was distilled to give 20·4 g (78%) acid chloride, b.p. 38°/0·14 mm.

4-Cyclohepten-1-yldiazomethylketone [δ = 5·37 ppm; ν_{max} 2110, 1645 cm^{-1}], prepared from the acid chloride in the manner described above, was decomposed by 3 different Cu catalysts: (a) by refluxing 3·0 g diazoketone in hexane with 8·0 g anhydrous $CuSO_4$ for 1 hr. The residual oil was distilled at 88°/0·15 mm to give 1·4 g II (55%); (b) by refluxing 4·5 g diazoketone in hexane with 16 g Cu powder for 3·5 hr to yield 1·8 g (47%) II; and (c) by refluxing 0·5 g diazoketone in either hexane or 50:50 acetonitrile–methanol with 2·0 g Cu I for 1 hr to yield mainly II as shown by g.l.p.c.

Pure II can be recrystallized from ether at dry ice temp, and sublimed, m.p. 126–128°. (Found: C, 78·9; H, 8·9. $C_9H_{12}O$ requires: C, 79·3; H, 8·9%).

Tricyclo[3.3.2.$0^{2,8}$]*decan*-3-*one* (III). A solution of 16.4 g of the diazoketone, 4-cyclohepten-1-yldiazomethylketone of the preceding experiment, in 25 ml dioxan was added dropwise to a stirred solution of 8·0 g freshly prepared Ag_2O, 21 g anhydrous Na_2CO_3 and 15 g $Na_2S_2O_3$ in 150 ml water at 70°. After 2·5 hr, the cooled reaction mixture was extracted with two 100-ml portions of ether (discarded), acidified with dil. HNO_3aq and extracted with four 150-ml portions of ether. Concentration of the dried ethereal solution afforded a residue which was distilled to give 12·2 g (80%) 4-cyclohepten-1-ylacetic acid, b.p. 104°/0·5 mm.

A solution of 6.8 g of this acid in 75 ml ether was treated dropwise with 4·0 g thionyl chloride and refluxed for 5 hr. Concentration and distillation afforded 5·3 g (70%) of the acid chloride, b.p. 48–49°/0·2 mm.

A solution of 1·5 g 4-cyclohepten-1-ylacetylchloride in 25 ml ether was added to a dried ethereal solution of diazomethane (from 2·9 g N-methyl-N-nitrosourea). After an initially vigorous evolution of gas the solution stood overnight protected by a $CaCl_2$ drying tube. Concentration afforded 1·3 g (85%) of diazoketone [δ = 5·22 ppm; ν_{max} 2109, 1645 cm^{-1}].

Decomposition was effected by adding 5·0 g 4-cyclohepten-1-ylmethyldiazo-methylketone in 10 ml purified n-hexane to a stirred suspension of 15 g anhydrous $CuSO_4$ in 75 ml hexane. After being stirred under reflux for 1 hr, the cooled solution was filtered and concentrated under red. press. Distillation afforded 2·4 g (47%) III, b.p. 104°/0·5 mm. Recrystallization from ether at dry ice temp, and sublimation gave tricyclo-[3.3.2.$0^{2,8}$]decan-3-one, m.p. 100–102°. Found: C, 79·5; H, 9·3. $C_{10}H_{14}O$ requires: C, 79·7; H, 9·3%).

Methanol-catalyzed ring expansion of II *to* III *with diazomethane.* A solution of diazomethane in 400 ml ether was prepared in the standard manner from 20 g N-methyl-N-nitrosourea. A solution of 3 g II in 100 ml MeOH was added to the solution of diazomethane and allowed to react at 4° for 3 days. The solvent was removed at red. press. and the resulting products were analyzed by g.l.p.c. Two major products were formed. The predominant one (ca. 65%) was identical in retention time and IR and NMR spectra to the sample of II prepared above. The second product, characterized by its IR and NMR spectra, is assumed to be the isomeric tricyclo[3.3.2.$0^{2,8}$]decan-4-one.

Tricyclo[3.3.1.$0^{2,8}$]*nona-3-one* (IV). Diethyl 2-cyclohexen-1-ylmalonate, b.p. 139–140·5°/8·0 mm, was saponified with alcoholic KOH to give the corresponding malonic acid in 87% of theory; m.p. 154–157°. Decarboxylation was effected by heating in pyridine at 95° for 4 hr to give 2-cyclohexen-1-ylacetic acid, b.p. 120–121°/8·0 mm; n_D^{23} 1·4795 (reported b.p. 125–127°/8 mm[28] and b.p. 120°/5 mm[29] and $n_a^{16.6}$ 1·4795[29]). The corresponding acid chloride was prepared with thionyl chloride: b.p. 74°/8·5 mm; n_D^{23} 1·4860 (amide, m.p. 149–150°; reported m.p. 147–148°[29,30]).

The diazoketone was prepared in the usual way [δ – 5·32 ppm; ν_{max} 2100, 1645 cm^{-1}] and was decomposed by boiling in hexane with anhydrous $CuSO_4$. Distillation gave IV, b.p. 107–111°/8·5 mm in 39% of theory from the acid chloride. The main component (91%) had a retention time of 18 min on a 13-ft, Anakrom ABS, 50–60 mesh column with 15% silicone oil 710 at 152° and a He flow of 100 cc/min. An oxime was prepared in the usual manner: m.p. 90–91°. (Found: C, 71.3; H, 8·7. $C_9H_{13}NO$ requires: C, 71·5; H, 8·7%).

Tricyclo[2.2.2.$0^{2,6}$]*octan-3-one* (V). 3-Cyclohexen-1-yldiazomethylketone was prepared through this sequence of intermediates: methyl 3-cyclohexene carboxylate,[15] 3-cyclohexene carboxylic acid[15,16] and 3-cyclohexene carbonyl chloride.[16] The diazoketone (ν_{max} 2111 and 1650 cm^{-1}) from 14·3 g of acid chloride was dissolved in 60 ml n-hexane and added dropwise over a period of 3 hr to the condensing pool of refluxing hexane whence it flowed to a stirred, refluxing slurry of 18 g Cu powder in 300 ml hexane. After an additional 4-hr period of reaction, the filtered solution was concentrated *in vacuo*. Distillation of the residue afforded 6·27 g material, b.p. 73–86°/7 mm. This material was purified by g.l.p.c. (4-m; 40/60 mesh kieselguhr; 20% Dow-Corning 710 silicone oil 150°; He at 200 ml/min). The yield of pure material was 31% of theory (λ_{max} 281 mμ, ε – 70 in 95% ethanol; NMR absorption at δ – 2·17, 2·07, 1·95, 1·75 and 1·65 ppm; semicarbazone derivative: m.p. 184–186°. These properties are to be compared with those reported by LeBel *et al.*:[17] λ_{max} 281 mμ, ε – 63 in 95% ethanol; NMR absorption at δ = 2·18, 2·09, 1·97, 1·77 and 1·65 ppm; semicarbazone derivative: m.p. 187·5–188°). Thanks to Professor LeBel's generosity in furnishing a sample of his material,[18] it could be established directly that the two samples had superimposable IR spectra and identical g.l.p.c. retention times.

Tricyclo[2.2.1.$0^{2,6}$]*heptan-3-one* (VI). 4-Bromocyclopentene was prepared according to the procedure developed by Bartlett and Rice[24] in which 3,5-dibromocyclopentene is reduced by $LiAlH_4$ (b.p. 43–48°/37 mm; reported[24] b.p. 43°/35 mm; same IR spectrum as that reported[24]).

The Grignard reagent from 24·4 g 4-bromocyclopentene was treated with CO_2 gas. Addition of 140 g ice and 35 ml conc. HCl, and extraction with ether gave an ethereal solution which was extracted with three 50-ml portions of 10% KOHaq. Acidification, extraction, concentration and distillation afforded 10·3 g (55%) cyclopentene-4-carboxylic acid; b.p. 135–142°/31 mm; anilide: m.p. 139–140° (reported b.p. 67°/14 mm;[19] anilide: m.p. 140°; m.p. 139–140°[22]).

The acid chloride was prepared by slow distillation in a vacuum-jacketed Vigreux column of a mixture of 1 molar equiv. of the acid and 2 molar equivs of benzoyl chloride (thionyl chloride[21] and oxalyl chloride[22] have also been used). The acid chloride, b.p. 84–85°/65 mm, was obtained in 72% of theory (28 g).

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The diazoketone was prepared in the usual manner by addition of the acid chloride in ether to 3 equivs of diazomethane in ether (ν_{max} 2109, 1650 cm^{-1}).

A solution of the diazoketone from 23·9 g acid chloride in 100 ml tetrahydrofuran was added through a high-dilution head over a 4·5-hr period to a stirred slurry of 700 ml boiling tetrahydrofuran and 25 g Cu powder. After being boiled and stirred an additional 2 hr, the solution was filtered, dried over $MgSO_4$, and concentrated on a steam bath to a residue from which 12·9 g (65%) nortricyclanone was obtained by distillation *in vacuo*; b.p. 72–79°/29 mm (95% of purity by g.l.p.c. on silicone or Carbowax 20 M). Redistillation in a vacuum-jacketed Vigreux column (3 to 1 reflux ratio) gave material with b.p. 75–77°/15 mm, n_D^{25} 1·4864, λ_{max} 285 mμ ($\varepsilon = 20$), and a 2,4-dinitrophenylhydrazine derivative, m.p. 185–187° with dec (reported b.p. 78–79°/24 mm;[26] n_D^{25} 1·4878;[26] 2,4-dinitrophenylhydrazone: m.p. 188·2–189·6°[25]). The IR spectrum (ν_{max} 3080, 3030, 2954, 2922, 2881, 1770 and 1755 cm^{-1}) and NMR spectrum (triplet (J = 5 c/s) at $\delta = 1{\cdot}14$ ppm; other lines at 2·10, 2·03, 1·92, 1·75 and 1·67 ppm) compares favourably with the reported IR spectrum[31] (ν_{max} 3078, 3032, 2951, 2918, 1768 and 1755 cm^{-1}) and NMR spectrum[32] (triplet J = 5 c/s. at $\delta = 1{\cdot}13$ ppm and another line at 1·8 ppm).

Reduction of the ketone (0·750 g) in 75 ml MeOH was effected by addition of a solution of $NaBH_4$ (0·262 g) in 30 ml MeOH, stirring the resulting mixture for 20 hr at room temp and boiling under reflux for 8 hr. Concentration at red. press., addition of 30 ml sat. $NaHCO_3$aq and extraction with ether gave an ethereal solution which was dried with $MgSO_4$, filtered and concentrated. Sublimation of the residue at 40°/10 mm afforded 0·421 g of tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol, m.p. 108–110°. A sample of this alcohol prepared independently by the method of Roberts *et al.*[25] melted from 104–106° even after repeated crystallization from pentane followed by sublimation. The IR spectra of the two samples were identical.

Photolysis of 1·00 g 3-cyclopenten-1-yldiazomethylketone was effected in solution in 200 ml purified, dried n-hexane in a Pyrex flask with a low-press. Hg-lamp. A white precipitate was formed at the wall nearest the source of light. The recovered product was shown by g.l.p.c. to consist of a large number of products. Although nortricyclanone could not be identified positively, a small band of the correct retention time had all the required IR absorptions along with additional bands.

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