B. By Alkylation with Methanol and Perchloric Acid.—5,5-Dimethyl-3-cyclohexylaminocyclohex-2-en-1-one (VIII, 0.00453 mole, 1.0 g.) in ether (30 ml.) and methanol (5 ml.) was treated with perchloric acid (1.5 ml.). The clear solution was evaporated and the residual oil crystallized from acetone–ether in Dry Ice–acetone to give a white solid, m.p. 111–120°. Three recrystallizations from aqueous ethanol gave 0.4 g. of colorless needles (38%), m.p. 174–176°, not depressed in admixture with authentic material above.

5,5-Dimethyl-3-(N-methylcyclohexylamino)cyclohex-2-en-1-one (IX).—A solution of 7.0 g. (0.05 mole) of 5,5-dimethylcyclohexane-1,3-dione and 5.7 g. (0.05 mole) of N-methylcyclohexylamine in 150 ml. of benzene was refluxed and water was removed azeotropically during 36 hr. Evaporation of the benzene gave 12 g. of red gum which on chromatography over alumina gave 5.3 g. (45%) of the enamino ketone IX. Recrystallization from methylcyclohexane gave yellow needles, m.p. 92–94°, $\lambda_{\max}^{\mathrm{EtOH}}$ 303 mμ (ε 32,500).

Anal. Calcd. for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.32; H, 10.61; N, 6.16.

5,5-Dimethyl-3-(N-methylcyclohexylamino)cyclohex-2-en-1-one Perchlorate (IX Perchlorate).—The enamino ketone IX above (1.2 g., 0.005 mole) in ethanol (10 ml.) was treated with 70% perchloric acid (2 ml.). Addition of water gave a crystalline perchlorate, m.p. 185–194°. Three crystallizations from aqueous ethanol gave pure material, m.p. 204–207°, $\lambda_{\max}^{\mathrm{EtOH}}$ 302 mμ (ε 28,000).

Anal. Calcd. for $C_{15}H_{26}ClNO_5$: C, 53.64; H, 7.80; N, 4.17; Cl, 10.56. Found: C, 53.65; H, 7.54; N, 3.99; Cl, 10.81.

Tributyl(5,5-dimethyl-3-oxocyclohex-2-en-1-yl)phosphonium Chloride (XI).—The chloro ketone X[12] (1.6 g., 0.01 mole) in methylcyclohexane (15 ml.) was treated with tributylphosphine (2.0 g., 0.01 mole) at the reflux temperature under nitrogen for 5 hr., during which time an oil came out of solution. After this was allowed to cool, the methylcyclohexane was decanted and the residual oil was washed with methylcyclohexane and benzene. Last traces of solvent were then removed by evaporation *in vacuo* to give 3.2 g. (89%) of the hygroscopic phosphonium chloride as an oil which solidified on standing. Two recrystallizations from ethyl acetate gave analytically pure material, m.p. 75–80°.

Anal. Calcd. for $C_{20}H_{38}ClOP$: C, 66.55; H, 10.61; Cl, 9.82; P, 8.58. Found: C, 66.45; H, 10.81; Cl, 9.64; P, 8.77.

The phosphonium chloride (1.5 g., 0.0042 mole) in ethanol (10 ml.) was poured into a solution of sodium tetraphenylboron (1.6 g., 0.0047 mole) in aqueous ethanol (15 ml.). There was an immediate precipitate of fine needles which was isolated by filtration to give 2.7 g. (100%) of the phosphonium tetraphenylborate, m.p. 185–189°. Two recrystallizations from ethyl acetate afforded analytically pure material, m.p. 190–192°.

Anal. Calcd. for $C_{44}H_{58}BOP$: C, 81.97; H, 9.07; P, 4.81. Found: C, 82.17; H, 9.27; P, 4.78.

The mesityl oxide and isophorone were obtained from Aldrich Chemical Co. and were redistilled before use.

Acknowledgment.—Thanks are due to Mr. F. B. Clarke for technical assistance.

[12] A. W. Crossley and H. R. LeSeuer, *J. Chem. Soc.*, **83**, 110 (1903).

Spirans. V.[1] Synthesis of Spiro Ketones Employing Enamines[2]

H. A. P. de Jongh, F. J. Gerhartl, and Hans Wynberg

Department of Organic Chemistry of the University, Bloemsingel 10, Groningen, The Netherlands

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The Stork addition of the pyrrolidine enamines of cyclopentanone and cyclohexanone to dibenzalacetone gave after hydrolysis the monoaddition products IVa and IVb. These could easily be cyclized *via* a Michael reaction to the diphenyl spiro ketones Va and Vb. Both spiro ketones were reduced to the spiro monoketones VIIa and VIIb, while VIIb was reduced to the diphenylspirohydrocarbon IX. The addition of cyclopentanone pyrrolidine enamine to dibenzalacetone, when carried out under vigorous conditions, gave the bridged product X, which contains the rare bicyclo[5.2.1]decane ring system.

In earlier publications the double Michael reaction between dibenzalacetone (II) and cyclohexane-1,3-diones, giving 7,11-diphenylspiro[5.5]undecane-1,5,9-triones in one step has been described.[1a,c] This paper deals with an extension of this reaction to the *mono* ketones, cyclopentanone and cyclohexanone, as donors.

The double Michael reaction between cyclohexanone itself and dibenzalacetone (II) was carried out under the same conditions as described earlier,[1a] *viz.*, with sodium ethoxide in ethanol. The spiro diketone Vb was indeed obtained in one step, but the highest yield amounted only to 5.3% and the reaction was attended by considerable tar formation, which made isolation of Vb tedious (see Experimental part). When the same reaction was carried out with cyclopentanone, only intractable tars were obtained. Great improvement was realized by using the pyrrolidine enamines of cyclopentanone and cyclohexanone as starting materials. The reaction between these enamines and dibenzalacetone was carried out as described by Stork, *et al.*,[3] for the reaction between cyclohexanone pyrrolidine enamine and ethyl vinyl ketone, *viz.*, in dioxane at room temperature. After hydrolysis with dilute acetic acid, the monoaddition products IVa and IVb were obtained in good yields. The physical constants, spectral data, and yields are recorded in Table I. The ultraviolet and infrared spectra correspond well with those of monobenzalacetone[4] [$\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (ε 20,900), $\nu_{C=O}$ 1673 and 1697 cm.$^{-1}$].

The "open-chain" products IVa and IVb could easily be cyclized *via* an intramolecular Michael reaction under the influence of sodium ethoxide in absolute ethanol. The spiro diketone Va was obtained after benzene extraction in 64% yield, while Vb crystallized immediately from the solution in 67% yield. Theoretically the cyclization of IVa and IVb could also take place on the other side of the carbonyl group, which would lead to bridged compounds. However, the spiro structure of Va is established unambiguously, because the alternative structure, namely the bridged compound X, could be prepared from IIIa (see below). The spiro structure of Vb is in accord with its reactions.

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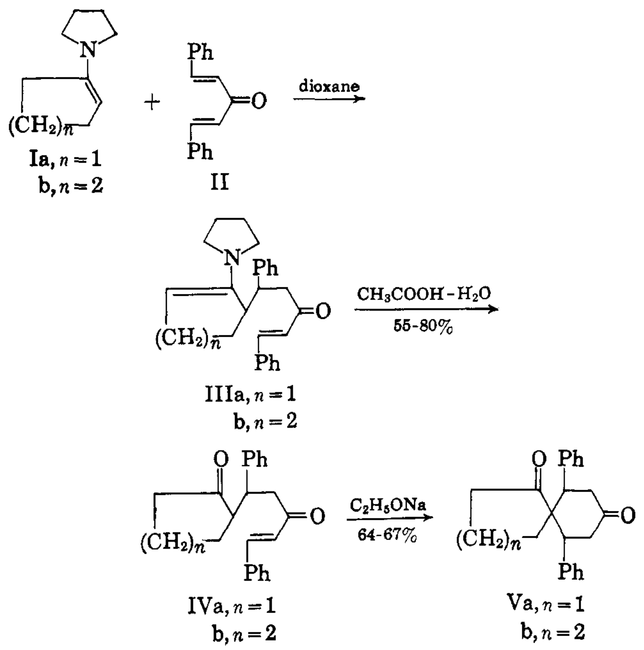
[1] (a) Part I: H. A. P. de Jongh and H. Wynberg, *Rec. trav. chim.*, **82**, 202 (1963). (b) Part II: H. A. P. de Jongh and H. Wynberg, *ibid.*, **82**, 602 (1963). (c) Part III: H. A. P. de Jongh and H. Wynberg, *Tetrahedron*, **20**, 2553 (1964). (d) Part IV: H. A. P. de Jongh and H. Wynberg, *ibid.*, **21**, 515 (1965).

[2] Partly taken from H. A. P. de Jongh, Ph.D. Thesis, Groningen, 1964.

[3] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[4] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).



Compound Vb was identical with the reaction product of cyclohexanone and dibenzalacetone under the influence of sodium ethoxide in ethanol. The ultraviolet and infrared spectra (Table I) show only the absorption of the unconjugated phenyl and carbonyl groups and are in excellent agreement with the spectra of the diphenyl spiro triketones described previously.[1a,c] Molecular models of Va and Vb show that the 1-carbonyl group (next to the spiro atom) is shielded considerably by the phenyl rings, while the other carbonyl groups are not. This is confirmed by the formation of monoethylene thioketals of Va and Vb, while the monoketones VIIa and VIIb do not give these derivatives at all.

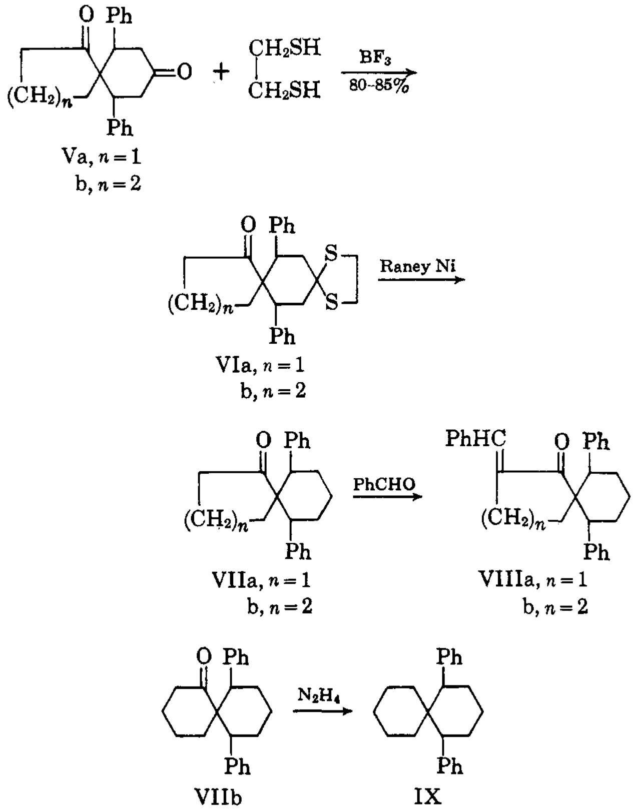
Table I

Yields and Physical Constants of Major Products

Compd.	% yield	M.p., °C.[a]	Infrared $\nu_{C=O}$, cm.$^{-1}$	Ultraviolet λ_{max}^{EtOH} mμ	Ultraviolet ε	Mol. wt. Found	Mol. wt. Calcd.
IVa	55	98	1726	292	24,100		
			1648				
IVb	80	137	1699	290	23,200		
			1644				
Va	64	119	1718	249	261	318[b]	318.4
			1699	253	333	320	
				259	420		
				265	345		
				299	123		
Vb	67	175	1695	248.5	266	330[c]	332.4
				253	348	338	
				259	441		
				265	366		
				298	103		
VIIa	96	113	1719	*d*			
VIIb	65	117.5	1700	*d*			
X	30	219	1726	248.5	590	324[b]	318.4
			1686	252.5	503	325	
				259	516		
				265	388		
				268	264		
				314	265		

[a] Only the upper limit is given. [b] Determined with a Mechrolab osmometer, Model 301A, in benzene. [c] Cryoscopic in camphor. [d] For ultraviolet spectra, see Experimental.

The spiro diketones Va and Vb could be reduced to the monoketones VIIa and VIIb by desulfurization of the ethylene thioketals VIa (m.p. 174–176°) and VIIb (m.p. 182.5–183.0°). The ethylene thioketal VIa has also been prepared in a higher over-all yield from IVa by treatment with BF_3–ether and ethane-1,2-dithiol in acetic acid solution (see Experimental part). The spiro monoketones could be converted into the benzal derivatives VIIIa [m.p. 106.5–109°, λ_{max}^{EtOH} 306 mμ (ε 24,600)] and VIIIb [m.p. 172–174°, λ_{max}^{EtOH} 292 mμ (ε 14,500)], whose ultraviolet spectra correspond well to that of benzalcyclohexanone [λ_{max}^{EtOH} 288 mμ (ε 19,000)]. The conversion to these benzal derivatives proves the existence of a methylene group adjacent to a carbonyl group in Va and Vb and thus supports their spiro structures.



The spiro ketone VIIb was converted to the hydrocarbon IX (m.p. 107.5–108°) *via* a Wolff–Kishner reduction.[5] When VIIa was subjected to the same reduction, no hydrocarbon could be isolated. The product, which was very insoluble in petroleum ether, probably resulted from a fission of the cyclopentanone ring.

When the reaction between the pyrrolidine enamine of cyclopentanone and dibenzalacetone was carried out under more vigorous conditions, *viz.*, boiling for 3.5 hr. in dioxane solution, a product different from IVa or Va was isolated after hydrolysis. The elementary analysis and molecular weight of this product (X), m.p. 217–218°, show it to be an isomer of Va, while the ultraviolet and infrared spectra do not differ appreciably from those of Va. In contrast to Va, which gives a mono-2,4-dinitrophenylhydrazone, the isomer X gave a bis-2,4-dinitrophenylhydrazone. Compelling evi-

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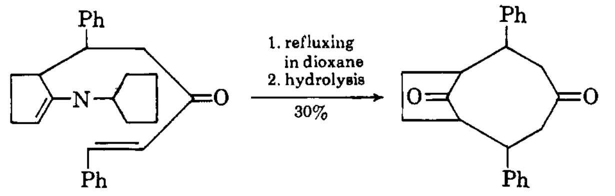
[5] D. H. R. Barton, A. da S. Campos-Neves, and A. I. Scott, *J. Chem. Soc.*, 2698 (1957).

dence will be given below that this new product must be X. The formation of this bridged product X is in accord with the well-established rule that *less* substituted enamine is formed from unsymmetrical ketones such as 2-alkylcycloalkanones.[3] An intramolecular Michael reaction of the monoalkylated enamine IIIa should then give X.

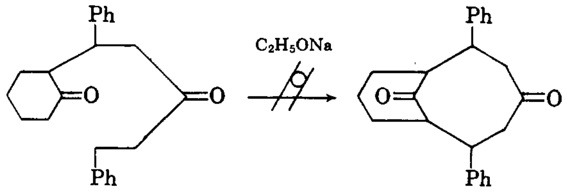


IIIa X

Compound X contains a rare bicyclic ring system, of which only one representative has been prepared by Gutsche, *et al.*, by the reaction between cyclohexanone and 1,4-bisdiazobutane.[6]

The assignment of the spiro diketone structure Va to the low-melting isomer and the bicyclic structure X to the high-melting isomer is supported by the following facts. The infrared spectra of both compounds show two carbonyl frequencies (Table I), the highest of which (1718–1726 cm.$^{-1}$) must be ascribed to the carbonyl group of the cyclopentanone ring[7] and the other (1682–1699 cm.$^{-1}$) to a carbonyl group of a cyclohexanone or cyclooctanone ring[7] (compare also the carbonyl frequencies of compounds IVa and IVb, Table I). Reduction of the low-melting isomer gives a monoketone with an infrared carbonyl frequency of 1719 cm.$^{-1}$; so the carbonyl group of this monoketone forms part of a cyclopentanone ring. The formation of a benzal derivative of this monoketone then excludes the bicyclic structure for the monoketone, because this structure contains no methylene group next to the cyclopentanone carbonyl group. Consequently, the monoketone must have structure VIIa and the low-melting diketone Va.

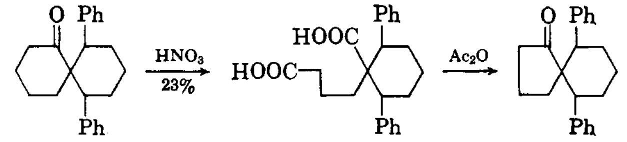
The formation of the bridged compound X *via* cyclization of the enamine prompted us to exclude the bridged structure XI for the cyclization product of the ketone IVb.



IVb XI

The formation of compound XI is unlikely because it contradicts the general observation that the Michael reaction between 2-methylcyclohexanone and α,β-ethylenic ketones gives 2-alkyl-2-methylcyclohexanones exclusively.[8] This is also demonstrated by the intramolecular Michael condensation of IVa to give the spiro diketone Va.

Finally, the spiro structure of Vb was proved unambiguously by the following conversions.



VIIb XII VIIa

Oxidation of the spiro ketone VIIb with nitric acid[9] gave the dicarboxylic acid XII (m.p. 213–216°) which, on treatment with acetic anhydride, following the method of Blanc,[10] furnished the spiro ketone VIIa. The latter was identical with the reduction product of Va as shown by identical infrared spectra and an undepressed mixture melting point.

Experimental

All melting points are uncorrected. The ultraviolet spectra were determined in 96% ethanol with a Zeiss spectrophotometer, Model P.M.Q. II. The infrared spectra from Table I were taken as KBr disks with a Perkin-Elmer spectrophotometer, Model 125; those recorded in this section were taken with a Perkin-Elmer Infracord, Model 137. The microanalyses and molecular weight determinations were carried out in the analytical section of our department under the direction of W. M. Hazenberg.

7,11-Diphenylspiro[5.5]undecane-1,9-dione (Vb). In One Step from Cyclohexanone.—To a solution of 10.0 g. (0.043 mole) of dibenzalacetone, m.p. 110.5–112°, and 4.2 g. (0.044 mole) of cyclohexanone, b.p. 155–156°, in 150 ml. of absolute ethanol, 3 ml. of a 5% solution of sodium in absolute ethanol was added. The yellow-brown solution was inoculated with some previously obtained material and kept at room temperature for 24 hr. No crystallization occurred, but keeping the red-brown solution for 15 hr. at 0° and 5 hr. at −20° resulted in the precipitation of 1.4 g. of gray product. Recrystallization from ethanol gave 0.7 g. of almost colorless 7,11-diphenylspiro[5.5]undecane-1,9-dione, m.p. 150–173°. The filtered reaction mixture was acidified with acetic acid and concentrated to 40 ml. After removal of much tarry material, first at room temperature, then at 0°, and finally at −20°, 0.8 g. of yellowish product, m.p. 150–170°, was obtained. Both crops of crude product (1.5 g.), after crystallization from ethanol, gave 0.75 g. (5.3%) of almost colorless spirodione, m.p. 174–175°.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28; mol. wt., 332.4. Found: C, 82.7, 83.0; H, 7.3, 7.3; mol. wt. (in camphor), 330, 338.

The compound unexpectedly gave a bis-2,4-dinitrophenylhydrazone, m.p. 159–163°.[11] In spite of repeated recrystallizations from ethyl acetate, no correct elementary analysis could be obtained.

Anal. Calcd. for $C_{35}H_{32}N_8O_8$ (692.7): C, 60.69; H, 4.65; N, 16.18. Found: C, 60.1, 60.1; H, 4.7, 4.7; N, 14.3, 14.3.

1,5-Diphenyl-5-(2-ketocyclopentyl)pent-1-en-3-one (IVa).—To a solution of 10.0 g. (0.043 mole) of dibenzalacetone, m.p. 110.5–112°, in 60 ml. of purified dioxane,[12] 5.9 g. (0.043 mole) of pyrrolidine enamine of cyclopentanone (prepared according to the method of Stork, *et al*,[3] b.p. 85–86° at 11 mm.) was added. The addition was attended by a marked rise in temperature, and, after 0.75 hr. at room temperature, the resulting enamine was hydrolyzed by heating under reflux with 15 ml. of 65% acetic acid for 15 min. The solvents were distilled *in vacuo* and the residual dark brown oil was taken up in 60 ml. of ethanol. After 4 hr. at 0°, 9.40 g. of brown crystalline material (m.p. 89–94.5°, with softening at 86°) was collected and washed with 20 ml. of petroleum ether (b.p. 40–60°). Two crystallizations from petroleum ether-benzene (15:1), using active carbon,

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(6) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 147–149.

(8) E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. Reactions*, **10**, 365 (1959).

(9) W. J. van Asselt and D. W. van Krevelen, *Rec. trav. chim.*, **82**, 51 (1963).

(10) H. G. Blanc, *Compt. rend.*, **144**, 1356 (1907); see also: L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1949, p. 130.

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

(12) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London, 1959, p. 177.

furnished 7.46 g. (55%) of almost colorless needles, m.p. 92–97°. Three additional crystallizations gave an analytically pure sample, m.p. 95–98°. The presence of a trace of bridged compound X was demonstrated by the occurrence of a small peak in the infrared spectrum of the crude product at 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{22}O_2$ (318.4): C, 82.98; H, 6.96. Found: C, 83.0, 83.0; H, 7.0, 7.2.

1,5-Diphenyl-5-(2-ketocyclohexyl)pent-1-en-3-one (IVb).—The pyrrolidine enamine of cyclohexanone[3] (6.5 g., 0.043 mole, b.p. 110–111.5° at 14 mm.) was added to a solution of 10.0 g. (0.043 mole) of dibenzalacetone, m.p. 110.5–112°, in 60 ml. of purified dioxane.[12] After 15 hr. at room temperature the resulting enamine was hydrolyzed with 20 ml. of 50% acetic acid, and the resulting crystals were collected after 1 hr. Recrystallization from 96% ethanol gave 11.30 g. (80%) of IVb, m.p. 133–136°. One more crystallization from ethanol raised the melting point to 136–137°.

Anal. Calcd. for $C_{23}H_{24}O_2$ (332.4): C, 83.10; H, 7.28. Found: C, 83.2, 83.2; H, 7.2, 7.2.

6,10-Diphenylspiro[4.5]decane-1,8-dione (Va).—A mixture of 10.75 g. (0.034 mole) of IVa, m.p. 86–98°, in 100 ml. of dry benzene and 80 ml. of methanol containing 0.5 g. of sodium was kept at room temperature for 16 hr. After the addition of 60 ml. of 10% acetic acid, the benzene layer was separated and the water layer was extracted twice with benzene. The combined organic layers were dried with $MgSO_4$, and the solvent was removed by distillation. The residual oil was taken up in 10 ml. of boiling acetic acid. After 1 day 4.30 g. of cyclized product, m.p. 112–119°, was collected and washed with 20 ml. of petroleum ether. A second crop of 2.65 g., m.p. 102–107°, was collected after concentration of the mother liquor. The total yield amounted to 6.95 g. (64%). Three additional crystallizations furnished pure Va as colorless plates, m.p. 117–119°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96; mol. wt., 318.4. Found: C, 83.1, 83.5; H, 6.8, 7.0; mol. wt. (determined with a Mechrolab osmometer, Model 301A in benzene), 320, 318.

The spiro diketone Va gave (even after heating under reflux for 3 hr.) only a mono-2,4-dinitrophenylhydrazone,[11] m.p. 179–183°. The infrared spectrum, taken as a Nujol suspension, showed a strong C=O peak at 1730 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{26}N_4O_5$ (498.5): C, 67.46; H, 5.25; N, 11.24. Found: C, 66.7, 66.9; H, 5.2, 5.3; N, 10.8, 10.8.

7,11-Diphenylspiro[5.5]undecane-1,9-dione (Vb). From IVb.—A solution of 3.51 g. (10.6 mmoles) of IVb, m.p. 133–136°, in 150 ml. of boiling absolute ethanol was cooled rapidly to 40°, when 3 ml. of a 5% solution of sodium in absolute ethanol was added. The mixture was cooled to 0° and kept at that temperature. Crystallization started almost at once and, after 1 night, 2.21 g. of Vb, m.p. 173–174.5°, was obtained. Neutralization (acetic acid) and concentration of the mother liquor gave another 0.132 g. of colorless product. The total yield was 2.34 g. (67%).

The spiro diketone showed no melting point depression upon admixture with Vb obtained from cyclohexanone in one step (see before), while the infrared spectra were identical.

8-Ethylene Thioketal of 6,10-Diphenylspiro[4.5]decane-1,8-dione (VIa).—Ethane-1,2-dithiol (10 ml.) and boron fluoride etherate (7 ml.) were added to a solution of 6.03 g. (19.0 mmoles) of Va, m.p. 102–119°, in 60 ml. of warm acetic acid (50°). Crystallization started almost at once and, after 1 night, 6.32 g. (85%) of VIa, m.p. 173–183°, was collected as long colorless needles. Crystallization from ethyl acetate raised the melting point to 179–183°. Two additional crystallizations gave pure VIa, m.p. 174–176°. The infrared spectrum, taken in Nujol suspension, showed a carbonyl peak at 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{26}OS_2$ (394.6): C, 73.06; H, 6.64; S, 16.26 Found: C, 73.3, 73.2; H, 6.6, 6.6; S, 16.1, 16.2.

8-Ethylene Thioketal of 6,10-Diphenylspiro[4.5]decane-1,8-dione (VIa). In One Step from IVa.—To a solution of 2.11 g. (6.63 mmoles) of IVa, m.p. 92–97°, in 20 ml. of glacial acetic acid, 3.5 ml. of boron fluoride etherate was added. The mixture was warmed at 60° for 0.5 hr., then 5 ml. of ethane-1,2-dithiol was added. After 3.5 hr. at 60°, an appreciable quantity of the thioketal had crystallized. After 1 day at room temperature, the yield was 1.77 g. (4.5 mmoles or 68%). The melting point (182–185°, softening at 178°) was 179–183° after crystallization from ethyl acetate. The mixture melting point with thioketal prepared from Va (m.p. 174–176°) was 183–184°.

9-Ethylene Thioketal of 7,11-Diphenylspiro[5.5]undecane-1,9-dione (VIb).—To a solution of 3.12 g. (9.7 mmoles) of Vb, m.p. 173–174.5°, in 50 ml. of glacial acetic acid, 3.5 ml. of ethane-1,2-dithiol and 3.5 ml. of boron fluoride etherate were added. After 1 night at room temperature, 3.16 g. (80%) of VIb was collected as colorless needles, m.p. 181.5–183°. Crystallization from ethyl acetate raised the melting point to 182.5–183°.

The infrared spectrum, taken in Nujol suspension, showed a carbonyl peak at 1710 cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{28}OS_2$ (408.6): C, 73.48; H, 6.91; S, 15.70. Found: C, 74.0, 73.8; H, 7.0, 6.9; S, 15.5, 15.3.

6,10-Diphenylspiro[4.5]decan-1-one (VIIa).—A solution of 3.83 g. (9.7 mmoles) of VIa, m.p. 179–183°, in 125 ml. of dioxane,[12] containing 40 g. of Raney nickel W_5,[13] was heated under reflux for 5 hr. After removal of the nickel and evaporation of the solvent, the resulting colorless glass was crystallized from ethanol. The yield of VIIa was 2.88 g. (96%), m.p. 111–114°. After two crystallizations the melting point was 111.3–113°. The ultraviolet spectrum showed maxima at 248.5 mμ (ε 260), 253.5 (347), 259 (435), 265 (333), and 303 (97).

Anal. Calcd. for $C_{22}H_{24}O$ (304.4): C, 86.80; H, 7.95. Found: C, 87.0, 87.0; H, 7.8, 7.9.

7,11-Diphenylspiro[5.5]undecan-1-one (VIIb).—The same procedure was followed as described for VIIa. Starting from 1.55 g. (3.8 mmoles) of VIb, m.p. 181.5–183°, 0.78 g. (65%) of VIIb was collected as colorless prisms, m.p. 114.3–116°. One additional crystallization from ethanol raised the melting point to 116.7–117.5°. The ultraviolet spectrum showed maxima at 248.5 mμ (ε 274), 253 (372), 259 (467), 265 (372), and 302 (63).

Anal. Calcd. for $C_{23}H_{26}O$ (318.4): C, 86.72; H, 8.23. Found: C, 86.9, 86.9; H, 8.3, 8.3.

7,11-Diphenyl-2-benzalspiro[5.5]undecan-1-one (VIIIb).—Using the method described by Johnson,[14] 0.5 ml. of a 15% sodium hydroxide solution was added to a solution of 284 mg. (0.89 mmole) of VIIb, m.p. 112.5–114°, in 5 ml. of ethanol. After warming and cooling, a clear solution was obtained, to which 1.1 ml. of benzaldehyde was added. After 4 days, 208 mg. (57%) of VIIIb, m.p. 163–166°, was collected as green-yellow feathery crystals. One crystallization from methanol, followed by one crystallization from petroleum ether (b.p. 60–80°)-benzene (5:1), raised the melting point to 172.5–174.0°. The ultraviolet spectrum showed a maximum at 292 mμ (ε 14,500). The infrared spectrum, taken in carbon tetrachloride, showed strong absorptions at 1680 (α,β-unsaturated carbonyl group) and 1600 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{30}H_{30}O$ (406.6): C, 88.61; H, 7.44. Found: C, 88.6, 88.6; H, 7.6, 7.7.

6,10-Diphenyl-2-benzalspiro[4.5]decan-1-one (VIIIa).—The reaction between VIIa and benzaldehyde was carried out as described above for the preparation of VIIIb. Starting from 190 mg. of crude VIIa, 142 mg. (58%) of green-yellow crystals of VIIIa, m.p. 104–109°, was obtained, after standing for 1 month. Crystallization from methanol raised the melting point to 106.5–109°. The ultraviolet spectrum showed a maximum at 306 mμ (ε 24,600). The infrared spectrum, taken in KBr, gave peaks at 1700 (α,β-unsaturated ketone) and 1625 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{29}H_{28}O$ (392.5): C, 88.73; H, 7.19. Found: C, 88.7, 88.4; H, 6.9, 7.1.

1,5-Diphenylspiro[5.5]undecane (IX).—The Wolff–Kishner reduction of VIIb was carried out after the modification described by Barton, *et al.*[5] To a solution of 0.7 g. of sodium in 15 ml. of diethylene glycol (b.p. 127.5–128° at 10 mm.), 363 mg. (1.09 mmoles) of VIIb (m.p. 114.3–116°) and 1.5 ml. of absolute hydrazine were added. The mixture was heated under reflux at 176–177° for 15 hr. Some liquid then was distilled until a temperature of 220° was reached, and refluxing was continued for 24 hr. at 210–220°. After cooling, 50 ml. of diluted hydrochloric acid was added. The almost colorless mixture was extracted twice with petroleum ether (b.p. 63–69°). After drying the extract with $MgSO_4$ and distillation of the solvent, 320 mg. of a colorless glass remained. Crystallization from methanol yielded 144 mg. (44%) of IX, m.p. 105–107°. One additional crystallization and two sublimations gave a pure sample, m.p. 107.5–108°. The ultraviolet spectrum showed maxima at 248.5 mμ (ε 286), 253.5 (397), 259 (491), 265 (384), and 268 (270).

Anal. Calcd. for $C_{23}H_{28}$ (304.4): C, 90.73; H, 9.27. Found: C, 90.8, 90.8; H, 9.2, 9.1.

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(13) H. L. Billica and H. Adkins in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 180.

(14) W. S. Johnson, *J. Am. Chem. Soc.*, **65**, 1323 (1943).

2,6-Diphenylbicyclo[5.2.1]decane-4,10-dione (X).—To a solution of 10.0 g. (0.043 mole) of dibenzalacetone, m.p. 110.5–112°, in 80 ml. of dioxane,[12] 5.9 g. (0.044 mole) of the pyrrolidine enamine of cyclopentanone[3] (b.p. 85–86° at 11 mm.) was added. After 1 night at room temperature, the mixture was refluxed for 3.5 hr. while moisture was excluded. The warm dark solution was treated with 10 ml. of concentrated hydrochloric acid, and then diluted with 100 ml. of water. The mixture was extracted three times with 100 ml. of benzene. The combined organic layers were washed with 100 ml. of water and the benzene was distilled *in vacuo*. To the partially crystalline residue 30 ml. of ether was added and 4.05 g. (30%) of greenish needles, m.p. 211–215°, were collected. Colorless X was obtained after two crystallizations from acetic acid, which raised the melting point to 217–218°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96; mol. wt., 318.4. Found: C, 82.8, 82.8; H, 7.1, 7.1; mol. wt., (determined with a Mechrolab osmometer, Model 301A in benzene), 324, 325.

The bis-2,4-dinitrophenylhydrazone of X was prepared by dissolving 400 mg. of X, m.p. 217–218°, in 150 ml. of boiling absolute ethanol, and adding 10 ml. of 2,4-dinitrophenylhydrazine solution.[11] After refluxing for 3 hr., the orange product was collected and thoroughly washed with absolute ethanol. The yield was 500 mg. (58%), melting at 251–253°.

Anal. Calcd. for $C_{34}H_{30}N_8O_8$ (678.6): C, 60.18; H, 4.45; N, 16.51. Found: C, 60.4, 60.2; H, 4.6, 4.6; N, 16.2, 16.3.

1-Carboxy-1-(3-carboxypropyl)-2,6-diphenylcyclohexane (XII). The oxidation of VIIb with nitric acid was performed following the modification described by van Asselt and van Krevelen.[9]

A solution of 1.417 g. (4.45 mmoles) of VIIb, m.p. 113–116°, in 40 ml. of acetic acid was added dropwise with stirring to 110 ml. of concentrated nitric acid, containing some ammonium vanadate and potassium nitrite. After 1 hr. at 35–40° and 1 hr. at room temperature the mixture was extracted with benzene. The benzene layers were extracted with diluted sodium hydroxide solution. After acidifying the alkaline layers with hydrochloric acid, the product was taken up in ether. The ethereal solution was dried with $MgSO_4$ and treated with active carbon. After evaporation of the solvent and crystallization from methanol, 378 mg. (23%) of XI was collected as colorless plates, m.p. 198–215°. Two additional crystallizations from methanol raised the melting point to 213–216° (softening at 198°).

Anal. Calcd. for $C_{23}H_{26}O_4$ (366.4): C, 75.39; H, 7.15. Found: C, 75.0, 74.9; H, 7.1, 7.3.

Cyclization of XII to VIIIa.—A solution of 160 mg. of XII, m.p. 198–215°, in 1 ml. of acetic acid anhydride was evaporated slowly at 140° in a small test tube. The bottom of the tube was placed in a metal bath. The temperature was maintained at 230° for 0.5 hr. and then raised to 330°. Most of the anhydride carbonized but some product settled at the upper part of the tube as a colorless glass. One crystallization of this glass from ethanol gave 17 mg. of material, m.p. 108–110°. The mixture melting point of this product with VIIa (m.p. 111.3–113°) was 109–112°. The infrared spectrum was identical with that of VIIa.

Twofold Terminal Alkylations of Disodio β-Diketones with Methylene Halides to Form Bis-β-diketones[1]

K. GERALD HAMPTON, ROBLEY J. LIGHT, AND CHARLES R. HAUSER

Department of Chemistry, Duke University Durham, North Carolina

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Disodiobenzoylacetone and certain related disodio β-diketones, prepared from the β-diketones by means of sodamide in liquid ammonia, underwent twofold alkylations at the terminal position with 1,3-dibromopropane and higher methylene halides to form bis-β-diketones. Some of the bis-β-diketones underwent twofold cyclizations with hydrazine to give dipyrazoles. Although the present method of synthesis of the bis-β-diketones failed with ethylene and methylene halides, it appears generally superior to twofold acylations of sodio ketones with diacid chlorides or diesters. Certain twofold alkylations of dipotassio β-diketones have afforded bis-β-diketones in lower yields than corresponding cases with disodio β-diketones. Disodioacetylacetone converted diphenyldichloromethane to tetraphenylethylene.

Previous papers have described alkylations of dipotassio β-diketones[2] and disodio β-diketones I (R = CH_3)[3,4] with alkyl halides to form terminal derivatives II.

$RCOCH(Na)COCH_2Na$ I

$RCOCH_2COCH_2R'$ II

The present paper describes twofold alkylations of disodio β-diketones I with 1,3-dibromopropane and appropriate higher methylene halides to give terminal bis-β-diketones IIIa–g (Table I).

$RCOCH_2COCH_2(CH_2)_nCH_2COCH_2COR$

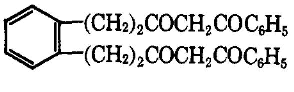
IIIa, $R = C_6H_5$; $n = 3$
b, $R = C_6H_5$; $n = 4$
c, $R = CH_3$; $n = 3$
d, $R = CH_3$; $n = 4$
e, $R = CH_3$; $n = 9$
f, $R = CH_3$; $n = 10$
g, $R = C_6H_5(CH_2)_2$; $n = 4$

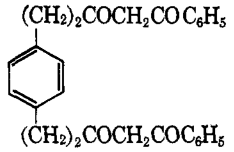
The procedure involved conversion of β-diketones to their disodio salts I by means of 2 mol. equiv. of sodamide in liquid ammonia and treatment of 2 (or slightly more) mol. equiv. of I with 1 of the methylene halide (eq. 1 and 2).

$$RCOCH_2COCH_3 \xrightarrow[\text{liq. }NH_3]{NaNH_2} I \tag{1}$$

$$2I \xrightarrow[2.\text{ acid}]{1.\ (CH_2)_nBr_2} \text{IIIa–g} \tag{2}$$

Similarly, twofold alkylations of I (R = C_6H_5) with α,α′-dibromo-*o*-xylene and α,α′-dichloro-*p*-xylene were effected to afford bis-β-diketones IV and V, respectively.


IV


V

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(1) Supported by U. S. Army Research Office (Durham).

(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958); R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **25**, 158 (1960).

(3) K. G. Hampton, T. M. Harris, and C. R. Hauser, *ibid.*, **30**, 61 (1965).

(4) Although the disodio β-diketone I is presumed to be an intermediate in these reactions, it has not yet been isolated in the pure crystalline form.