

**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,<sup>12</sup> 5.9 g. (0.044 mole) of the pyrrolidine enamine of cyclopentanone<sup>3</sup> (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.<sup>11</sup> 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.<sup>9</sup>

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 VIIIa.

## Twofold Terminal Alkylations of Disodio $\beta$ -Diketones with Methylene Halides to Form Bis- $\beta$ -diketones<sup>1</sup>

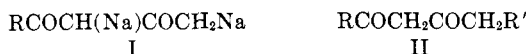
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Received December 2, 1964

Disodiobenzoylacetone and certain related disodio  $\beta$ -diketones, prepared from the  $\beta$ -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- $\beta$ -diketones. Some of the bis- $\beta$ -diketones underwent twofold cyclizations with hydrazine to give dipyrazoles. Although the present method of synthesis of the bis- $\beta$ -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  $\beta$ -diketones have afforded bis- $\beta$ -diketones in lower yields than corresponding cases with disodio  $\beta$ -diketones. Disodioacetylacetone converted diphenyldichloromethane to tetraphenylethylene.

Previous papers have described alkylations of dipotassio  $\beta$ -diketones<sup>2</sup> and disodio  $\beta$ -diketones I ( $R = CH_3$ )<sup>3,4</sup> with alkyl halides to form terminal derivatives II.

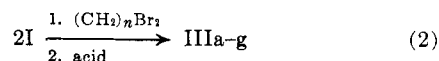
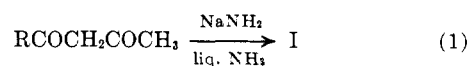


The present paper describes twofold alkylations of disodio  $\beta$ -diketones I with 1,3-dibromopropane and appropriate higher methylene halides to give terminal bis- $\beta$ -diketones IIIa–g (Table I).

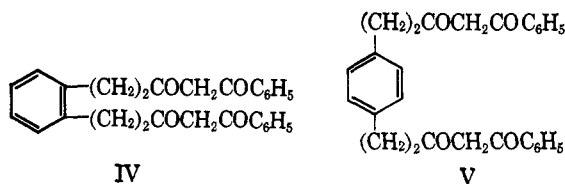


- IIIa,  $R = C_6H_5$ ;  $n = 3$   
 b,  $R = C_6H_5$ ;  $n = 4$   
 c,  $R = CH_3$ ;  $n = 3$   
 d,  $R = CH_3$ ;  $n = 4$   
 e,  $R = CH_3$ ;  $n = 9$   
 f,  $R = CH_3$ ;  $n = 10$   
 g,  $R = C_6H_5(CH_2)_2$ ;  $n = 4$

The procedure involved conversion of  $\beta$ -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).



Similarly, twofold alkylations of I ( $R = C_6H_5$ ) with  $\alpha, \alpha'$ -dibromo-*o*-xylene and  $\alpha, \alpha'$ -dichloro-*p*-xylene were effected to afford bis- $\beta$ -diketones IV and V, respectively.



(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  $\beta$ -diketone I is presumed to be an intermediate in these reactions, it has not yet been isolated in the pure crystalline form.

TABLE I  
 TWOFOLD ALKYLATIONS OF DISODIO SALT I WITH METHYLENE HALIDES TO FORM BIS- $\beta$ -DIKETONES<sup>a</sup>

Disodio salt I		Dihalide		Bis- $\beta$ -diketone			
R	Moles	Formula	Moles	No.	Recrystn. solvent	M.p., °C.	Yield, %
C <sub>6</sub> H <sub>5</sub>	0.20	(CH <sub>2</sub> ) <sub>3</sub> Br <sub>2</sub>	0.10	IIIa	Methanol	62-63 <sup>b</sup>	58
C <sub>6</sub> H <sub>5</sub>	0.10	(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.05	IIIb	Benzene-methanol	108-109 <sup>c</sup>	89
CH <sub>3</sub>	0.63	(CH <sub>2</sub> ) <sub>3</sub> Br <sub>2</sub>	0.30	IIIc	Ethanol	66-67.5	69-78 <sup>d</sup>
CH <sub>3</sub>	0.42	(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.20	IIId	Methanol	72-73	80 <sup>e</sup>
CH <sub>3</sub>	0.05	(CH <sub>2</sub> ) <sub>9</sub> Br <sub>2</sub>	0.025	IIIe	Ethanol	84-85	81
CH <sub>3</sub>	0.05	(CH <sub>2</sub> ) <sub>10</sub> Br <sub>2</sub>	0.025	IIIf	Ethanol	85.5-86.5	73
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub>	0.10	(CH <sub>2</sub> ) <sub>4</sub> Br <sub>2</sub>	0.05	IIIg	Methanol-ethanol	48.5-50	38
C <sub>6</sub> H <sub>5</sub>	0.05	C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> Br) <sub>2-o</sub>	0.025	IV	Benzene	94-95 <sup>f,g</sup>	65
C <sub>6</sub> H <sub>5</sub>	0.10	C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> Cl) <sub>2-p</sub>	0.05	V	Benzene	132-133 <sup>h,i</sup>	67

<sup>a</sup> These compounds gave a red enol test with 95% ethanolic ferric chloride. <sup>b</sup> Lit.<sup>5</sup> m.p. 64.5-65.5°. <sup>c</sup> Lit.<sup>5</sup> m.p. 107.5-108°. <sup>d</sup> When the ratio of I to dihalide was 2:1, the yield of IIIc was 63%. <sup>e</sup> When the ratio of I to dihalide was 2:1, the yield of IIId was 73%. <sup>f</sup> Lit.<sup>6</sup> m.p. 95-96°. <sup>g</sup> Copper chelate m.p. 253-254°; lit.<sup>6</sup> m.p. 254°. <sup>h</sup> Lit.<sup>6</sup> m.p. 128-129°. <sup>i</sup> Copper chelate m.p. 303-305°; lit.<sup>6</sup> m.p. 305°.

 TABLE II  
 ANALYSES OF NEW BIS- $\beta$ -DIKETONES

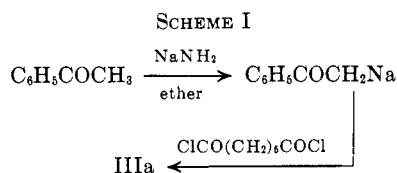
Bis- $\beta$ -diketone	Formula	Calcd., %		Found, %		Infrared peaks, $\mu$
		C	H	C	H	
2,4,10,12-Tridecanetetron (IIIc)	C <sub>13</sub> H <sub>20</sub> O <sub>4</sub>	64.98	8.39	64.90	8.36	6.20
2,4,11,13-Tetradecanetetron (IIId)	C <sub>14</sub> H <sub>22</sub> O <sub>4</sub>	66.11	8.72	66.20	8.93	6.25
2,4,16,18-Nonadecanetetron (IIIe)	C <sub>19</sub> H <sub>32</sub> O <sub>4</sub>	70.33	9.94	70.30	9.84	6.09
2,4,17,19-Eicosanetetron (IIIf)	C <sub>20</sub> H <sub>34</sub> O <sub>4</sub>	70.97	10.13	70.99	10.09	6.20
1,16-Diphenyl-3,5,12,14-hexadecanetetron (IIIg)	C <sub>28</sub> H <sub>34</sub> O <sub>4</sub>	77.39	7.89	77.40	7.74	6.23, 12.7, 14.5

 TABLE III  
 DIPYRAZOLES OF BIS- $\beta$ -DIKETONES

Dipyrzole	Recrystn. solvent	M.p., °C.	Yield, %	Formula	Calcd., %			Found, %		
					C	H	N	C	H	N
VIa	Aq. methanol	93-94.5	96 <sup>a</sup>	C <sub>13</sub> H <sub>20</sub> N <sub>4</sub> ·H <sub>2</sub> O	63.37	8.86	22.38	63.45	8.68	22.46
VIb	Aq. methanol	72-73	90 <sup>a</sup>	C <sub>14</sub> H <sub>22</sub> N <sub>4</sub> ·H <sub>2</sub> O	63.60	9.15	21.20	63.65	9.02	21.20
VIc	Acetic acid	205-207	72	C <sub>24</sub> H <sub>28</sub> N <sub>4</sub>	77.80	7.07	15.12	77.63	7.08	15.01
VII	Benzene <sup>b</sup>	253-254	95	C <sub>28</sub> H <sub>34</sub> N <sub>4</sub>	80.36	6.26	13.39	80.35	6.22	13.43

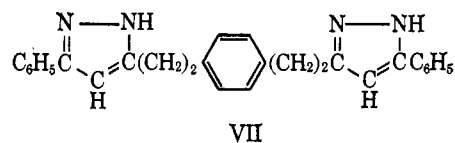
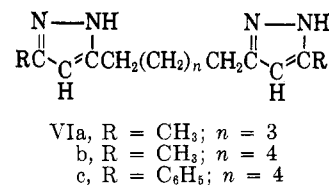
<sup>a</sup> The melting point of the product of which the yield was based was slightly lower than the recorded value. <sup>b</sup> The crude product was triturated in the solvent.

The results are summarized in Tables I-III. Bis- $\beta$ -diketones IIIa-b, IV, and V are known compounds<sup>5,6</sup>; they were identified by essential agreement of their melting points and of the melting points of the copper chelates (for IV and V) with the reported values (see Table I). Also, IIIa was independently synthesized as described previously (Scheme I).<sup>5</sup>



The structures of the bis- $\beta$ -diketones IIIc-g, which appear to be new compounds, were supported by analogy, by analysis (see Table II), and by twofold cyclizations (for IIIc and IIId) with hydrazine to form dipyrzoles VIa and b. Also, two of the known bis- $\beta$ -diketones IIIb and V were converted to dipyrzoles VIc and VII, respectively. Apparently VIa and b were isolated as hydrates (see Table III).

Table I shows that the yields of the bis- $\beta$ -diketones were generally good to excellent (58-89%) and some of them could probably be improved. At least in certain



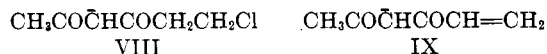
cases the use of a calculated 5% excess of disodio salt I over that required in the 2:1 ratio of I to methylene halide (see eq. 2) is recommended (compare yields of IIIc and d in the body of Table I with those in footnotes d and e). This method appears generally superior to that involving twofold acylations of sodio ketones with diacid chlorides or diesters. Thus the twofold acylations of sodioacetophenone with pimelyl chloride (Scheme I) and diethyl suberate have afforded bis- $\beta$ -diketones IIIa and b in yields of only 25 and 5%, respectively.<sup>5</sup>

However, the present method failed with ethylene and methylene halides. The reaction of disodio  $\beta$ -diketones I with ethylene chloride appeared to involve  $\beta$ -elimination since much of the  $\beta$ -diketone was recovered, but that with ethylene bromide seemed to follow also another course of reaction (see Experi-

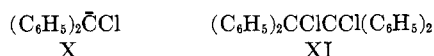
(5) D. F. Martin, M. Shamma, and W. C. Fernelius, *J. Am. Chem. Soc.*, **80**, 4891 (1958).

(6) M. M. Coombs and R. P. Haughton, *J. Chem. Soc.*, 5015 (1961).

mental). The reaction of I ( $R = CH_3$ ) with methylene chloride afforded much tarry material, which might possibly have arisen by monoalkylation,  $\beta$ -elimination, and polymerization through intermediate monoanions VIII and IX or their neutral analogs.



Disodio salt I ( $R = CH_3$ ) converted dichlorodiphenylmethane to tetraphenylethylene in 70% yield; also two unidentified products were obtained. The tetraphenylethylene might possibly have arisen by displacement on halogen, alkylation, and dechlorination through intermediates X and XI.<sup>7</sup> Another possible course of reaction would involve the intermediate formation of diphenylcarbene; this seems less likely since benzhydryl chloride has been observed to undergo self alkylation through X under similar conditions.<sup>8</sup>



It should be mentioned that twofold alkylations of dipotassiobenzoylacetone with the appropriate dihalides to form bis- $\beta$ -diketones IV and V have been reported previously.<sup>6</sup> However, the yields were only 15–25%, which are much lower than those obtained by us employing disodiobenzoylacetone (see Table I). Similarly, in an initial experiment by us with dipotassiobenzoylacetone and 1,3-dibromopropane, bis- $\beta$ -diketone IIIc was produced in 40% yield, which was somewhat lower than that (63%) realized with the disodio salt under similar conditions (see footnote *d*, Table I). Such a metallic cation effect has recently been observed also in monoalkylations of certain dialkali  $\beta$ -diketones with alkyl halides to form II.<sup>3</sup>

### Experimental<sup>9</sup>

**Disodio  $\beta$ -Diketone I.**—Disodiobenzoylacetone ( $I$ ,  $R = C_6H_5$ ) was prepared by addition of solid benzoylacetone (from an erlenmeyer flask through Gooch tubing) to a stirred suspension of 2 mol. equiv. of sodamide<sup>10</sup> in 400–700 ml. of commercial, anhydrous liquid ammonia (at  $-33^\circ$ ). After 30 min., the disodio salt was employed in the condensations described below.

**Disodio-6-phenyl-2,4-hexanedione [I,  $R = C_6H_5(CH_2)_2$ ]** was prepared similarly, except that a solution of the  $\beta$ -diketone<sup>3</sup> in 20 ml. of ether was added to the suspension of sodamide.

**Disodioacetylacetone (I,  $R = CH_3$ )** was prepared from acetylacetone and sodamide in liquid ammonia and some ether at  $-78^\circ$  under nitrogen as described recently.<sup>3</sup> The reaction mixture was allowed to warm to  $-33^\circ$  before being employed in the condensations.

**Twofold Alkylations of Disodio Salts I with Dihalides to Form Bis- $\beta$ -diketones.**—To a stirred solution of the disodio  $\beta$ -diketone in 400–700 ml. of liquid ammonia was added, during 10 min., a solution of 0.5 mol. equiv. of the methylene halide in 20 ml. of ether (the xylene halides were added as solids). After 1 hr., 250 ml. of ether was added, and the reaction mixture was placed

(7) Such displacements on halogen are well known, and a similar dechlorination ( $\beta$ -elimination) of hexachloroethane by diphenylmethide ion has been observed in this laboratory: unpublished result of W. G. Kofron and C. R. Hauser.

(8) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

(9) Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are corrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn., and Dr. Ing. A. Schoeller Mikro-Labor, Kronach, West Germany. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord using the potassium bromide pellet method for solids.

(10) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

on the steam bath. When the liquid ammonia had evaporated, the resulting suspension was cooled in ice, and a mixture of 100 g. of crushed ice and excess (30–40 ml. for 0.05–0.4 mole of I) of cold, concentrated hydrochloric acid was added. The two layers were separated. The ethereal layer was combined with three ethereal extracts of the aqueous layer, and the solvent was evaporated. The residue was recrystallized from an appropriate solvent. In the preparations of bis- $\beta$ -diketones IIIb, IIIe, IIIf, IV, and V, the acidified ether-aqueous mixture was filtered before separation of the two layers. The solid obtained on the funnel was combined with the residue left after evaporation of the ether, and the mixture was recrystallized. The results are summarized in Tables I and II.

**Independent Synthesis of Bis- $\beta$ -diketone IIIa (Scheme I).**—This reaction was effected as described previously<sup>3</sup> to give, after several recrystallizations from methanol, 2 g. (17%) of IIIa, m.p. 62–63°. A mixture melting point with a sample of IIIa obtained through twofold alkylation as described above (see Table I) was not depressed. Also the infrared spectra of the two samples were identical.

**Cyclizations of Bis- $\beta$ -diketones with Hydrazine to Form Dipyrzoles.**—To a solution of 1 g. of bis- $\beta$ -diketone in 20 ml. of 95% ethanol was added 20 drops of 95% hydrazine. After the solution had refluxed for 1 hr., the solution was cooled, and cold water was added. The resulting precipitate was collected and recrystallized from an appropriate solvent to afford the dipyrzole. The results are summarized in Table III.

**Reactions of Disodio Salts I with Ethylene and Methylene Halides.**—Disodio salt I ( $R = C_6H_5$ ) (0.20 mole) was treated with 0.1 mole of ethylene chloride or bromide and the reaction mixture was worked up in the usual manner. Only recovered benzoylacetone was isolated. When the reaction of 0.20 mole each of disodio salt I ( $R = CH_3$ ) and ethylene chloride was effected, there were recovered 71% of the acetylacetone and a trace of the ethylene chloride. When the reaction of 0.20 mole each of disodio salt I ( $R = CH_3$ ) and ethylene bromide was effected, there were recovered 12.5 g. of a mixture (b.p. 53–58° at 55 mm.) of acetylacetone and ethylene bromide in about equal amounts (indicated by v.p.c.); another fraction of the reaction product (5 g., b.p. 155–158° at 4 mm.) contained two unidentified compounds (indicated by v.p.c.). A tarry pot residue was obtained.

Disodio salt I ( $R = CH_3$ ) (0.2 mole) was treated with 0.1 mole of methylene chloride and the reaction mixture was worked up in the usual manner. There was obtained much tarry material which resisted attempts to dissolve it in various solvents.

**Reaction of Disodio Salt I ( $R = CH_3$ ) with Dichlorodiphenylmethane.**—Disodioacetylacetone (0.20 mole) was treated with dichlorodiphenylmethane (0.10 mole). After 30 min., ether was added, and the ammonia was evaporated. The resulting ethereal suspension was shaken with ice and hydrochloric acid, and the mixture was filtered. The solid on the funnel was combined with the residue obtained on evaporating the ethereal layer of the filtrate, and the mixture was recrystallized from benzene to give 11.6 g. (70%) of tetraphenylethylene, m.p. 223–224°, undepressed on admixture with an authentic sample of tetraphenylethylene.<sup>8</sup> The infrared spectra of the two samples were identical.

In another experiment on the same scale, the ethereal layer of the filtrate obtained on filtering the acidified reaction product was extracted with 1 *N* sodium hydroxide, and the alkaline extract was acidified. The resulting mixture was extracted with ether, and the ethereal extract was evaporated to give 3.0 g. of material, m.p. 103–119° and at 122–124° after recrystallizations from ethanol. The infrared spectrum of this product showed bands at 705 and 790  $\text{cm}^{-1}$  and a broad band at 1640  $\text{cm}^{-1}$  indicating the presence of phenyl and  $\beta$ -diketone groups, respectively.<sup>11</sup> Also, on standing, the aqueous layer of the filtrate of the original acidified reaction mixture precipitated 0.15 g. of material, m.p. 275–277° after recrystallization from benzene. The infrared spectrum of this material indicated the absence of the phenyl group.

**Twofold Alkylation of Dipotassiobenzoylacetone with 1,3-Dibromopropane.**—Acetylacetone (0.20 mole) was converted to its dipotassiobenzoyl salt by means of potassium amide<sup>2</sup> (0.40 mole) in 500 ml. of liquid ammonia, and the resulting salt was treated with

(11) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 76, 77, 142.

1,3-dibromopropane (0.10 mole) as described above for the sodio salt I. The reaction afforded 9.5 g. (40%) of IIIc, m.p. 60–65° after one recrystallization from petroleum ether (b.p. 30–60°). After one recrystallization from aqueous methanol

and three from *n*-hexane, the melting point was raised to 66–67.5°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>: C, 64.98; H, 8.39. Found: C, 64.88; H, 8.55.

## Synthesis of 3-Hydroxy-4-nitro-5-arylcyclohexanones by Claisen Condensation and Cyclization Reactions with $\beta$ -Aryl- $\gamma$ -nitro Ketones

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*Received October 15, 1964*

Examples are given of a novel, base-catalyzed ester acylation and cyclization reaction through which the  $\gamma$ -nitro ketones, obtained by Michael addition of nitromethane to benzalacetones, are converted to 3-hydroxy-4-nitro-5-arylcyclohexanones, some of which may be dehydrated to corresponding nitro enones.

The purpose of this paper is to report the finding of a novel synthesis of 4-nitrocyclohexanones, typically III, IV, and V in Chart I. Recent general interest in aliphatic nitro compounds,<sup>1–3</sup> including some precursors of hydrophenanthridines,<sup>4,5</sup> prompts now the presentation of these reactions, which were developed in 1961 in an effort to find a synthetic approach to 1-aryl-2-nitrocyclohexanes different from the well-known diene addition to  $\omega$ -nitrostyrenes.<sup>4–7</sup> It seems possible that synthetic routes *via* such nitro compounds to precursors of alkaloids in the lycorine, crinine, and caranine series ultimately may be more flexible than schemes involving Pschorr cyclization<sup>8,9</sup> or reactions of resorcinols with *o*-bromobenzoyl compounds.<sup>10,11</sup>

Although sodionitroalkanes usually react with two molecules of a very reactive, low molecular weight,  $\alpha,\beta$ -unsaturated ketone, nitrile, etc.,<sup>1,12</sup> the Michael addition of nitroalkanes to the less reactive benzylidene malonates, nitriles, and ketones generally is mono,<sup>12–20</sup> giving, in the latter case,  $\gamma$ -nitro ketones such as II. In addition to known IIa,<sup>16</sup> two other  $\gamma$ -nitro ketones, IIb and IIc, have now been prepared by addition of nitromethane to the appropriate benzylideneacetones.

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For this reaction, sodium methoxide<sup>13–16</sup> was found to be superior to ammonia<sup>18</sup> or amines.<sup>17,19</sup> The I  $\rightarrow$  II condensation also is smoother than some alternative methods<sup>12</sup> which were given preliminary trial, for example, Michael addition of reactive methylene compounds to  $\omega$ -nitrostyrenes and addition of sodionitromethane to cinnamates or arylidenecyanoacetates; neither of these reactions was found well adapted to synthesis of  $\beta$ -aryl- $\gamma$ -nitro carbonyl compounds in which the benzene ring bears oxy substituents.

A high-melting by-product, identified as VIc, was always isolated along with IIc in the reaction of methylenedioxybenzalacetone (Ic) with sodionitromethane. The formation of VIc eventually was minimized by employing a severalfold excess of sodionitromethane. There are no less than four conceivable ways in which VIc might arise during the reaction Ic  $\rightarrow$  IIc or, as was occasionally found subsequently, during other base-catalyzed, further reactions of IIc. These are (1) direct condensation of piperonal (formed by reverse Michael or aldol reactions) with IIc; (2) formation of dipiperonalacetone and its cyclic Michael reaction with nitromethane anion; (3) reverse Michael reaction of IIc (acetone loss) to form the  $\omega$ -nitrostyrene, followed by addition of Ic and ring closure; and (4) bis Michael addition involving two molecules of Ic and one of nitromethane, followed by similar acetone loss through reverse Michael reaction, and ring closure. It is not possible at present to decide which one (or several) of these four is responsible for formation of VIc. Similar by-products (VIa,b) were not found in the sodionitromethane reactions of Ia and Ib.

In trial experiments it soon was found, as expected, that in order to promote fairly complete Claisen reactions of compounds II there had to be used at least 2, and preferably 3 or 4, equiv. of base and a similar or greater excess of acylating esters in each case. Apparently this is because of the relative ease with which the CH<sub>2</sub>NO<sub>2</sub> group initially forms its corresponding anion, so that additional base is then required to promote the (presumably less facile) formation of CO–CH<sub>2</sub><sup>–</sup>. Experiments with ethyl oxalate, of all the esters tried, were the most consistently successful, the products, obtained in fairly good yields, being cyclic hydroxynitro keto esters, IV. Ester exchange, from the ethyl of ethyl oxalate to methyl of the sodium methoxide used in excess, was observed in all three of the reactions leading to isolated compounds IV.