azulene and 26 mg. (69% net yield) of 1-chloro-3-bromoazulene, m.p. 76–77°, which was identical (mixed melting point and infrared spectrum) with the material obtained in A.

1-Bromo-3-nitroazulene (XII). A. From 1-Nitroazulene.—A solution of 54 mg. (0.30 millimole) of N-bromosuccinimide in 7 ml. of dry benzene was added to 52 mg. (0.30 millimole) of 1-nitroazulene dissolved in 5 ml. of dry benzene. A test with starch–iodide paper was negative after 9 hours and the reaction mixture was filtered through a short alumina column. The column was washed with benzene and the filtrate concentrated under reduced pressure. The brown-violet residue was transferred to an alumina column with a few ml. of methylene chloride and the chromatogram developed and eluted with benzene. A brown-red zone separated from a very weak red zone and the former was collected, concentrated and rechromatographed. Removal of the solvent from the desired eluate fraction gave 75 mg. (99%) of brownish lavender crystals, m.p. 181–182°. A single recrystallization from methylene chloride–petroleum ether raised the melting point to 183–184°. The ultraviolet spectrum of an alcohol solution showed maxima in mμ at 222, log ε 4.40; 278, log ε 4.36; 317, log ε 4.27; 410, log ε 4.06[3] and the visible spectrum of a solution in three parts of methylene chloride and seven parts of alcohol had a single broad maximum at 532 mμ, ε 1071. The infrared spectrum was recorded.[3]

Anal. Calcd. for $C_{10}H_6BrNO_2$: C, 47.64; H, 2.40; Br, 31.70. Found: C, 47.40; H, 2.55; Br, 31.86.

B. From 1-Bromoazulene.—To a solution of 60 mg. (0.29 millimole) of 1-bromoazulene in 5 ml. of acetic anhydride cooled in a Dry Ice–acetone-bath was added, with stirring, a suspension of 75 mg. (0.31 millimole) of cupric nitrate trihydrate in 5 ml. of acetic anhydride over a period of 5 minutes. After an additional 5 minutes the cooling bath was removed and the mixture stirred for 30 more minutes during which time the color became purple. The reaction was quenched with 20 ml. of water, the mixture shaken with an additional 100 ml. of water and the separated organic layer extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed twice with dilute ammonium hydroxide and water, the solvent removed under reduced pressure and the residue chromatographed on an alumina column with 20% methylene chloride–80% petroleum ether as the eluent. Three zones (blue, brown-red and weak red) developed. From the blue eluate fraction was recovered 20 mg. of the bromoazulene. Rechromatography of the material from the brown-red fraction yielded 23 mg. (47% net yield) of 1-bromo-3-nitroazulene, m.p. 181–182°, which was identical (mixed melting point and infrared spectrum) with the product obtained in A.

N-Acetyl-3-bromo-1-azulylamine (XIII). A. From 1-Bromo-3-nitroazulene.—To a mixture of 72 mg. (0.286 millimole) of 1-bromo-3-nitroazulene, 15 ml. of acetic acid and 5 ml. of acetic anhydride was added, with stirring, 0.3 g. of zinc dust in small portions. The color of the solution changed from red to greenish blue. Stirring was continued for 1 hour, water was added and the mixture extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed with cold 3 *N* ammonium hydroxide, then water and the solvent removed. The green residue was chromatographed on an alumina column with methylene chloride as the eluent. Removal of the solvent from the eluate containing the greenish blue fraction left a green solid which crystallized from petroleum ether–acetone; yield 63 mg. (83%). The product melted with decomposition at 145–150°. The ultraviolet spectrum of an alcohol solution displayed maxima at 241 mμ, log ε 3.40 and 294 mμ, log ε 4.42.[3] The visible spectrum of a solution in absolute methanol had a single broad maximum at 650 mμ, ε 365. The infrared spectrum of a nujol suspension was taken.[3]

Anal. Calcd. for $C_{12}H_{10}BrNO$: C, 54.56; H, 3.82; Br, 30.26. Found: C, 54.89; H, 3.60; Br, 30.28.

B. From N-Acetyl-1-azulylamine (VI).—A solution of 34 mg. (0.18 millimole) of N-acetyl-1-azulylamine in 10 ml. of dry benzene and 2 ml. of methylene chloride was treated with 34 mg. (0.19 millimole) of N-bromosuccinimide dissolved in 5 ml. of dry benzene. The mixture, which gave a negative starch–iodide test within a few minutes, was filtered through a short alumina column and the column washed with methylene chloride. The product (42 mg., 86%) was identical (infrared spectrum) with that obtained in A and was isolated in the same manner.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

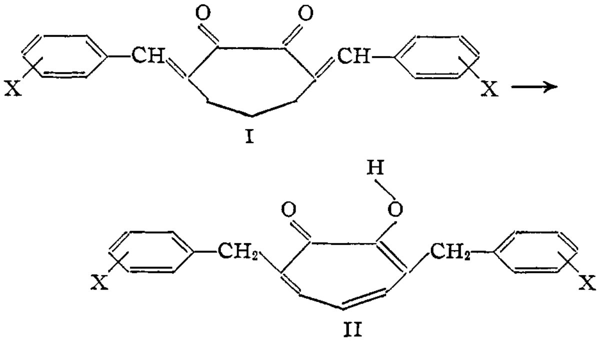
Tropolones by Isomerization. II. Substituted 3,7-Dibenzyltropolones[1,2]

BY NELSON J. LEONARD AND JAMES W. BERRY

RECEIVED JUNE 4, 1953

The isomerization of substituted 3,7-dibenzylidene-1,2-cycloheptanediones to the correspondingly substituted 3,7-dibenzyltropolones has been effected in triethylene glycol solution using palladium-on-charcoal. The general method has been shown to possess advantages over the isomerization as effected by hydrogen bromide–acetic acid or by palladium-on-charcoal without solvent. The ultraviolet absorption spectra of the substituted 3,7-dibenzylidene-1,2-cycloheptanediones have been related to those of the correspondingly substituted chalcones. The spectra of the substituted 3,7-dibenzyltropolones bear close resemblance to each other and to those of other known tropolones.

The finding that 3,7-dibenzylidene-1,2-cycloheptanedione (Ia) can be isomerized to 3,7-dibenzyltropolone (IIa) by means of hydrogen bromide–acetic acid[3] caused us to investigate the suggested generality of this new synthesis of tropolones. Accordingly, representative substituted 3,7-dibenzylidene-1,2-cycloheptanediones (I, also the analogous 3,7-di-(*m,p*-dimethoxybenzylidene) and 3,7-difur-



a, X = H; b, X = *p*-CH_3; c, X = *p*-CH_3O; d, X = *o*-Cl; e, X = *p*-NO_2

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(1) The major portion of this paper was presented at the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 15, 1952.

(2) This work was supported by a grant from E. I. du Pont de Nemours and Company, Inc., and by a grant from the Research Board of the University of Illinois.

(3) N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2143 (1953).

TABLE I

ULTRAVIOLET AND INFRARED ABSORPTION SPECTRA

Compounds	Ultraviolet										Infrared Wave number, cm.$^{-1}$	
1,2-Cycloheptanediones	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	Conj. C═O	Conj. C═C and aromatic
3,7-Dibenzylidene (Ia)[3]	313[a]	4.46					209	4.91			1683[c]	1605, 1578, 1500
3,7-Di-(*p*-methylbenzylidene) (Ib)	328[a]	4.40			∼237	4.12					1685[d]	1600, 1517
3,7-Di-(*p*-methoxybenzylidene) (Ic)	352[a]	4.54	∼299[f]	4.25	∼244 229	4.23 4.26					1678[d]	1589, 1515
3,7-Di-(*o*-chlorobenzylidene) (Id)	299[a]	4.22					203	4.52			1684[d]	1608, (755)
3,7-Di-(*p*-nitrobenzylidene) (Ie)	...[e]										1685[d]	1609, 1595, 1519
3,7-Di-(*m*,*p*-dimethoxybenzylidene)	365[a]	4.34	∼310	4.14	236	4.20	204	4.53			1679[d]	1593, 1585, 1520
3,7-Difurfurylidene	358[a]	4.65	∼312	∼4.32			208	4.78			1677[d]	1600, 1549
Tropolones											Bonded OH	Carbonyl
3,7-Dibenzyl (IIa)[3]	372[b]	3.66	360	3.67	324	3.64	252 ∼242	4.29 4.24			2990[c]	1605
3,7-Di-(*p*-methylbenzyl) (IIb)	372[b]	3.83	360	3.84	322 ∼313	3.90 3.88	241	4.43	215	4.49	2940[c]	1600
3,7-Di-(*p*-methoxybenzyl) (IIc)	372[b]	3.93	361	3.93	322 ∼310 ∼283 ∼277	3.92 3.91 4.07 4.09	243	4.55	224	4.60	2940[c]	1611
3,7-Di-(*o*-chlorobenzyl) (IId)	372[b]	3.82	359	3.82	322 ∼310	3.82 3.78	248	4.42	214	4.40	2945[c]	1603
3,7-Di-(*p*-nitrobenzyl) (IIe)	...[e]										2960[c]	1605

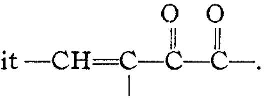
[a] 95% ethanol, [b] cyclohexane, [c] chloroform = solvent. [d] Nujol mull. [e] Very limited solubility. [f] ∼ Denotes inflection point.

furylidene compounds) were made and were subjected to the isomerizing conditions of hydrogen bromide–acetic acid. Isomeric products (*i.e.*, tropolones) resulted from Ib, d and e, but the yields (36, 25 and 15%, respectively) were not as satisfactory as for the isomerization of the parent diketone (Ia) to 3,7-dibenzyltropolone (IIa). Moreover, the method was not applicable to compounds containing an ether function.

We therefore turned to the use of palladium catalysts, encouraged by the known aromatization of 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol in the presence of palladium,[4] as well as by means of hydrogen bromide–acetic acid.[3,5] 3,7-Dibenzyltropolone (IIa) was obtained in 80% yield by heating a mixture of 3,7-dibenzylidene-1,2-cycloheptanedione (Ia) with 10% palladium-charcoal catalyst at 250° and subliming the product from the reaction mixture. This method also provided respectable yields (80, 56%) of tropolones IIb and IIc, but its usefulness appeared to be limited to those tropolones which could be readily sublimed from the solid reaction mixture. The most general method and that providing the highest yields of tropolones has now been found to be aromatization with palladium-on-charcoal using triethylene glycol as a solvent. Triethylene glycol was selected as the most advantageous solvent due to its stability under the reaction conditions, the possibility of convenient regulation of reaction temperature, and the solubility of triethylene glycol in water, making possible the facile separation of the reaction product. In this solvent, with palladium-on-charcoal at 280°, 3,7-dibenzylidene-1,2-cycloheptanedione (Ia) was converted to 3,7-dibenzyltropolone (IIa) in 90% yield, and substituted 3,7-dibenzyltropolones (IIb, c, d, e) were likewise obtained in very satisfactory yields.

The structure of 3,7-dibenzyltropolone (IIa) has been firmly established[3] and thus serves as a model for the structure of each of the aromatization products obtained in the series: I → II. In the absence of proof of structure by unequivocal synthesis[3] of the other members of the series (IIb, c, d, e), a number of pertinent facts can be marshalled for the positive identification of these products as tropolones. Thus, the substituted 3,7-dibenzylidene-1,2-cycloheptanediones (Ib, c, d, e), prepared by condensation of the appropriately substituted benzaldehyde with 1,2-cycloheptanedione, are bright yellow solids, whereas the products are much lighter in color. Ultimate analyses indicate that the products are isomeric with the starting materials. Methanolic solutions of the products gave with ferric chloride a dark red color which changed to a brilliant dark green on the addition of excess ferric chloride.[6,7] The spectra (Table I) of the starting materials and products are strikingly different, and the infrared and ultraviolet absorption spectra of the products are characteristic of tropolones[6,8,9] and especially similar to those of 3,7-dibenzyltropolone.[3]

In consideration of the ultraviolet absorption spectra of the substituted dibenzylidenediketones and dibenzyltropolones (Table I), a number of relationships are indicated. To begin with, there are striking differences in the ultraviolet maxima of the diketones I, indicative of the conjugation of the substituted phenyl group with the unit


$—CH{=}\underset{|}{C}—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—$

. By contrast, when these diketones have undergone isomerization to the correspondingly substituted dibenzyltropolones II, all of the latter show striking similarity in their ultraviolet absorption maxima. All have bands at 372, 360, 322 and 243 mμ, indicative of the tropo-

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[4] E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

[5] R. Weiss and J. Ebert, *Monatsh.*, **65**, 399 (1935).

[6] J. W. Cook and J. D. Loudon, *Quart. Revs.*, **5**, 99 (1951).

[7] The product of isomerization of 3,7-di-(*p*-nitrobenzylidene)-1,2-cycloheptanedione was exceptional in that it gave a red color only.

[8] H. P. Koch, *J. Chem. Soc.*, 512 (1951).

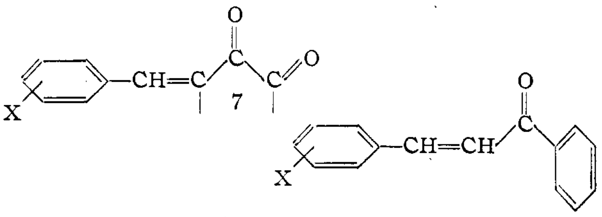
[9] G. P. Scott and D. S. Tarbell, THIS JOURNAL, **72**, 240 (1950).

lone absorbing unit and its insulation (by CH_2) from the substituted phenyl groups.

The earlier postulate[10] that the 3-benzylidene-1,2-diketone system represents an absorbing unit comparable with chalcone receives support from a comparison of the long wave length ultraviolet maxima of the substituted 3,7-dibenzylidene-1,2-cycloheptanediones with those of the correspondingly substituted chalcones (Table II). The maximum for 3,7-dibenzylidene-1,2-cycloheptanedione lies almost exactly at the same wave length as that for chalcone. Moreover, the shifts caused by the introduction of similar substituents into the benzene rings in each series are practically identical throughout (see Table II). The agreement between the long wave length absorption maxima is not as striking for 3,7-difurfurylidene-1,2-cycloheptanedione compared with furfurylideneacetophenone (β-2-furylacrylophenone).

TABLE II

LONG WAVE LENGTH ULTRAVIOLET ABSORPTION MAXIMA[a]



3,7-Dibenzylidene-1,2-cycloheptanediones X	λ, mμ	λ, mμ	Chalcones[11] X
H	313	312	H
p-CH_3	328	333	*p*-CH_3
p-CH_3O	352	348	*p*-CH_3O
o-Cl	299	298	*o*-Cl
m,p-di-CH_3O	365	365	*m,p*-OCH_2O
3,7-Difurfurylidene-1,2-cycloheptanedione	358	341	β-2-Furylacrylophenone

[a] In 95% ethanol.

Experimental[12]

Absorption Spectra.—The infrared absorption spectra were obtained with a Perkin–Elmer automatic recording infrared spectrometer, model 21. The ultraviolet absorption spectra were determined using a Cary recording spectrophotometer, model 11.

Substituted 3,7-Dibenzylidene-1,2-cycloheptanediones.—The general method of synthesis involved heating a solution of 5 millimoles of 1,2-cycloheptanedione,[13] 20 millimoles of the appropriate aldehyde, and 5 drops of piperidine[3,14,15,16] in absolute ethanol (sufficient to dissolve, at least 5 ml.) at the reflux temperature for four hours. The product which separated when the reaction mixture was cooled was usually recrystallized from acetone (ethanol–acetone for Ib, methyl ethyl ketone–ethyl acetate for Id, nitromethane for Ie).

3,7-Di-(*p*-methylbenzylidene)-1,2-cycloheptanedione (Ib), yellow prisms, m.p. 172–172.5°, yield 18%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.55; H, 6.82.

3,7-Di-(*p*-methoxybenzylidene)-1,2-cycloheptanedione (Ic), yellow prisms, m.p. 176–177°, yield 14%.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.13; H, 6.26.

3,7-Di-(*o*-chlorobenzylidene)-1,2-cycloheptanedione (Id), yellow prisms, m.p. 233–235°, yield 15%.

Anal. Calcd. for $C_{21}H_{16}Cl_2O_2$: C, 67.94; H, 4.34. Found: C, 68.05; H, 4.45.

3,7-Di-(*p*-nitrobenzylidene)-1,2-cycloheptanedione (Ie), yellow prisms, m.p. 276–277°, yield 29%.

Anal. Calcd. for $C_{21}H_{16}N_2O_6$: C, 64.29; H, 4.11; N, 7.14. Found: C, 64.23; H, 4.11; N, 7.39.

3,7-Di-(*m,p*-dimethoxybenzylidene)-1,2-cycloheptanedione, yellow plates, m.p. 176–177°, yield 8%.

Anal. Calcd. for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 70.93; H, 6.15.

3,7-Difurfurylidene-1,2-cycloheptanedione, yellow prisms, m.p. 171–171.5°, yield 28%.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.47; H, 5.20.

Isomerization. A. Hydrogen Bromide–Acetic Acid.—This method was applied to Ib, d and e under the conditions described[3] for the conversion of 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone.

B. **Palladium-on-charcoal.**—A mixture of 3.5 g. (12 millimoles) of 3,7-dibenzylidene-1,2-cycloheptanedione and 2.0 g. of 10% palladium–charcoal catalyst was heated under *ca.* 17 mm. pressure for 1.25 hours at 250°. The 3,7-dibenzyltropolone was sublimed from the reaction mixture at 250° and 0.3 mm., and the sublimate was recrystallized from methanol as colorless needles, m.p. 118–119°, yield 2.8 g. (80%), identical with the compound produced by hydrogen bromide–acetic acid isomerization.[3] This method also converted Ib to IIb and Ic to IIc.

C. **Palladium-on-charcoal in Triethylene Glycol.**[17] **3,7-Dibenzyltropolones.**—A mixture of 7 millimoles of the 3,7-dibenzylidene-1,2-cycloheptanedione (unsubstituted or substituted) and 1.0 g. of 10% palladium–charcoal catalyst in 25 ml. of triethylene glycol was heated under reflux at 280° for 1.5–3.0 hours. The reaction mixture was cooled, filtered and the filtrate was diluted with 100 ml. of water. The aqueous mixture was extracted with ether (hot cyclohexane was used for IIa and IIe), the combined ether extracts were dried and decolorized, and the ether was evaporated. The residual solid was then recrystallized.

3,7-Dibenzyltropolone (IIa), cream-colored or near colorless needles from cyclohexane, m.p. 118–119°, undepressed on admixture with authentic material, yield 90%.

3,7-Di-(*p*-methylbenzyl)-tropolone (IIb), cream-colored needles from methanol, m.p. 116–118°, yield 83%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.71; H, 6.89.

3,7-Di-(*p*-methoxybenzyl)-tropolone (IIc), cream-colored needles from cyclohexane, m.p. 101.5–102.5°, yield 67%.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.36; H, 6.11.

3,7-Di-(*o*-chlorobenzyl)-tropolone (IId), tan needles from methanol, m.p. 109–112°, yield 25%.

Anal. Calcd. for $C_{21}H_{16}Cl_2O_2$: C, 67.94; H, 4.34. Found: C, 68.12; H, 4.59.

3,7-Di-(*p*-nitrobenzyl)-tropolone (IIe), cream-colored needles from tetrahydrofuran–methanol, m.p. 222.5–223°, yield 30%.

Anal. Calcd. for $C_{21}H_{16}N_2O_6$: C, 64.29; H, 4.11; N, 7.14. Found: C, 64.24; H, 4.16; N, 7.24.

The reaction product from the attempted aromatization of 3,7-di-(*m,p*-dimethoxybenzylidene)-1,2-cycloheptanedione was an oil which gave a green color with ferric chloride but could not be induced to crystallize. No tropolone was obtained from 3,7-difurfurylidene-1,2-cycloheptanedione by any of these isomerization procedures.

URBANA, ILLINOIS

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[10] N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2714 (1953).

[11] H. H. Szmant and A. J. Basso, *ibid.*, **74**, 4397 (1952).

[12] All melting points are corrected. We wish to thank Mr. Samuel Gelfand for his assistance. We are indebted to Miss Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth for microanalyses, and to Miss Helen Miklas, Mrs. Robert Hill and Mrs. Bruce Burnett for determination of the absorption spectra.

[13] R. W. Vander Haar, R. C. Voter and C. V. Banks, *J. Org. Chem.*, **14**, 836 (1949).

[14] P. Karrer and C. Cochand, *Helv. Chim. Acta*, **28**, 1181 (1945).

[15] H. Schlenk, *Ber.*, **81**, 175 (1948).

[16] H. Schlenk, *ibid.*, **85**, 901 (1952).

[17] This is the method of preference.