merized to yield polymers of varying properties depending on the functionality of the epoxide monomer.

The triamide of 1,2,4-butanetricarboxylic acid was prepared by ammonolysis of the triethyl ester.

EXPERIMENTAL

General procedure for esterification of 1,2,4-butanetricarboxylic acid. A mixture of 3 moles of alcohol (or less if only mono- or diester is desired), 190 g. (1 mole) of 1,2,4-butanetricarboxylic acid, 500 g. of toluene, and 5 g. of *p*-toluenesulfonic acid was heated to reflux and water removed azeotropically. The reaction mixture was washed with one-third volume of 5% sodium bicarbonate solution and then with one-third volume of water. Solvent was removed by distillation at reduced pressure and the ester obtained by distillation or as a stripped residue product.

Vinylation method. Bis(3-cyclohexenylmethyl) vinyl 1,2,4-butanetricarboxylate. A mixture of 300 g. (0.795 mole) of bis(3-cyclohexenylmethyl) hydrogen 1,2,4-butanetricarboxylate, 500 ml. of toluene, 5 g. of zinc oxide, and 8 g. of anhydrous zinc acetate was charged to a 3-l. "316" stainless steel bomb in a rocking furnace. The system was purged five times with nitrogen to 75 p.s.i.g. at room temperature. Nitrogen was added to 25 p.s.i.g. and the system was heated to 160° with rocking. Nitrogen was added to 130 p.s.i.g., then acetylene was added to 300 p.s.i.g. Reaction occurred at 178° and the pressure was maintained at 280–300 p.s.i.g. by addition of acetylene. After 6 hr. at 178–191°, the gas uptake ceased. After cooling the system the reaction mixture was discharged, the catalyst removed by filtration, and the filtrate washed twice with 10% sodium carbonate solution to remove unreacted acid and then washed with water. Hydroquinone (0.5 g.) was added and the toluene was removed by distillation. The product was taken as a residual dark colored oil in 82% yield (n_D^{20} 1.4958, d_{20}^{20} 1.1058).

Anal. Calcd. for $C_{23}H_{32}O_6$: C, 68.3; H, 7.97. Found: C, 68.8; H, 7.76.

General procedure for epoxidation of unsaturated esters. Tri-(2,3-epoxy-2-ethylhexyl) 1,2,4-butanetricarboxylate. A solution (915 g.) of 21.5% peracetic acid in ethyl acetate was added dropwise to tri(2-ethyl-2-hexenyl) 1,2,4-butanetricarboxylate (309 g.) at 50° over a period of 90 min. After an additional 3 hr. at 50°, analysis of the mixture for peracetic acid indicated that the reaction was complete. The reaction mixture was then fed dropwise to an equal volume of ethylbenzene which was refluxing in a 24 inch × 1 inch glass helix-packed column at 25–30 mm. As the reaction mixture was fed to the kettle, ethyl acetate, acetic acid, and excess peracetic acid together with ethylbenzene were taken off overhead. After the volatiles had been removed, the kettle contents were filtered to remove a small amount of suspended matter, and tri(2,3-epoxy-2-ethylhexyl) 1,2,4-butanetricarboxylate was obtained as a residue product having the following properties: 6.75% oxirane oxygen (80% purity), 0.31% acid (calculated as acetic acid), iodine value (Wyj's method) 1.09, color less than 1 Gardner 1933.

Preparation of 1,2,4-butanetricarboxamide. Anhydrous ammonia was bubbled through a stirred mixture of 409 g. of triethyl 1,2,4-butanetricarboxylate (1.5 moles) in 500 g. of ethylene glycol at 59–60° over 38 hr., at which point 96 g. of ammonia (5.65 moles) had been adsorbed. The crude product mixture was freed of excess ammonia, byproduct ethanol, and glycol by evaporation under reduced pressure at ambient temperature. The residual crystalline mass was taken up in hot dimethylformamide, treated with decolorizing carbon, filtered, and cooled to crystallize. After filtration, the semidry product was washed with ethyl ether and dried to give 143 g., a 51.6% yield, of fine white crystals (m.p. 195–196°) of 1,2,4-butanetricarboxamide.

Anal. Calcd. for $C_7H_{13}N_3O_3$: C, 44.91; H, 7.00; H, 22.45. Found: C, 45.18; H, 7.09; N, 22.50.

Acknowledgment. The authors are grateful to Messrs. G. R. Arnold, T. F. Carruthers, C. N. Dailey, H. R. Dodd, C. A. Gibson, and R. E. Gothard for technical assistance.

SOUTH CHARLESTON, W. VA.

---

(3) K. Freudenberg and J. Geiger, *Ann.*, **575**, 145 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Enamines of 2-Indanones[1a,b]

ALFRED T. BLOMQUIST AND EMIL J. MORICONI[2a,b]

Received April 11, 1961

Enamines 2-(*N*-pyrrolidyl) (IIa), 2-(*N*-piperidyl) (IIb), 2-(*N*-hexamethyleneimino) (IIc), and 2-(*N*-morpholinyl)indene (IId) were prepared from 2-indanone and the appropriate *sec*-amines; similarly 3-phenyl-2-(*N*-hexamethyleneimino)indene was obtained from 1-phenyl-2-indanone (VIII). C-Alkylation of IIa–IId with bromomethyl benzyl ether was highest with IIc. 1-Methyl (V), 1-benzyloxymethyl- (VI), and 1-benzyl-2-indanone (VII) were prepared by C-alkylation of IIc with the appropriate alkyl halide. A shift of 108–131 cm.$^{-1}$ in the double bond stretching maximum was observed in going from IIa–IId to their respective ternary iminium salts. Selenium dioxide oxidation of VIII and 3-phenyl-1-indanone gave, respectively, 1-hydroxy-1-phenyl-2-indanone and 3-hydroxy-3-phenyl-1,2-indandione, and 3-phenylindone. Nitrosation of V and VI under alkaline conditions gave no α-oximinoindanones but unexpectedly yielded ring expanded products tentatively identified as alkylated 3-hydroxyisoquinoline *N*-oxides.

Enamine C-alkylation and acylation is now firmly established as a signal addition to the methods available for the preparation of α-substituted ketones from carbonyl compounds.[3] In this paper we report on the preparation, alkylation, and absorption spectra of enamines of 2-indanones

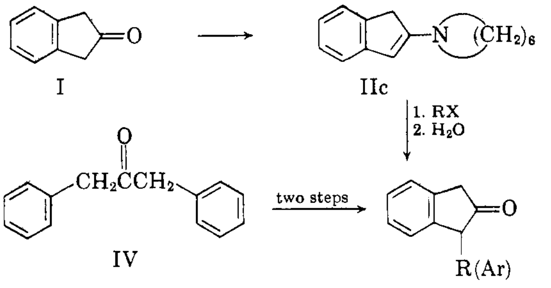
---

(1)(a) Sponsored by the United States Air Forces under Contract No. AF 49(638)688 monitored by the Air Force Office of Scientific Research of the Air Research and Development Command. (b) Presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(2)(a) Air Research and Development Command Postdoctoral University Research Associate, 1959–1960. (b) On leave of absence from Fordham University, N. Y., N. Y.

and their salts, and discuss some reactions of 1- and 2-indanone derivatives.

2-Indanone (I) was converted to enamine 2(*N*-hexamethyleneimino)indene (IIc) in 85% yield. IIc was alkylated with methyl iodide, bromomethyl benzyl ether, and benzyl bromide to give, respectively, 1-methyl- (V), 1-benzyloxymethyl- (VI), and 1-benzyl-2-indanone (VII) as oils in yields of 20–40%.[4] 1-Phenyl-2-indanone[5] (VIII) was prepared in 71% yield from 1,3-diphenyl-2-propanone (IV). Enamine 3-phenyl-2-(*N*-hexamethyleneimino)indene (IX) was prepared from VIII in 59%



V. R = CH_3
VI. R = $CH_2OCH_2C_6H_5$
VII. R = $CH_2C_6H_5$
VIII. Ar = C_6H_5

yield. All enamines were characterized by analyses, spectra, and conversion to perchlorate salts.

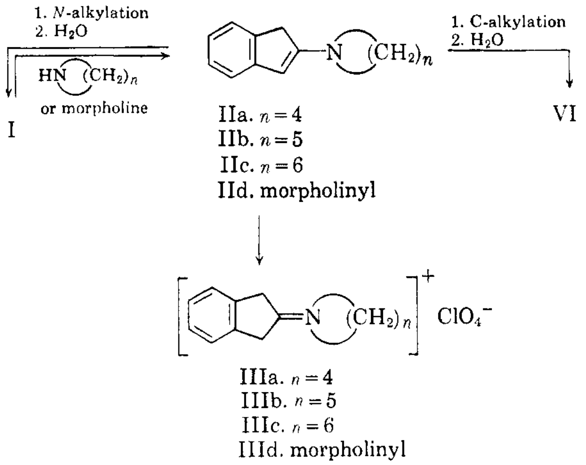
Enamines possess two different reactive positions and can be considered ambident molecules which undergo electrophilic reaction to form C- or *N*-alkylated intermediates.[6] Hydrolysis of these intermediates would yield, respectively, the desired 1-alkylated-2-indanones (V–VII), or I. We have made a comparative study of C- *vs.* *N*-alkylation of enamines IIa–IId with bromomethyl benzyl ether and the results are summarized in Table I. The enamine 2-(*N*-hexamethyleneimino)indene (IIc) gave optimum yields (39%) of C-alkylated product (VI) and was therefore used in all alkylations.

TABLE I

C- vs. N-ALKYLATION OF IIA–IID WITH BROMOMETHYL BENZYL ETHER[a]

Enamine	Yield, % C-Alkylation, VI	 *N*-Alkylation, I[b]
IIa	8	14
IIb	22	7
IIc	39	0
IId	25	0

[a] See Experimental for details. [b] This represents the percent yield of I directly recovered on fractional distillation; a high boiling fraction is also obtained which may contain 2-indanone condensation products.



Selenium dioxide oxidation of 1-phenyl-2-indanone (VIII) gave 1-hydroxy-1-phenyl-2-indanone (XI)[7] and 3-hydroxy-3-phenyl-1,2-indandione (XII) in 6% and 11% yields, respectively. A shorter reaction time increased the yield of XI (9%) and correspondingly lowered the yield of XII (3%). Selenium dioxide oxidation of 3-phenyl-1-indanone (XIII) gave a 60% yield of 3-phenylindone (XIV) isolated as its semicarbazone. In neither oxidation was the diketone 3-phenyl-1,2-indandione (XVI) isolated.[8,9]

---

(3) (a) See M. E. Kuehne, *J. Am. Chem. Soc.*, **81**, 5400 (1959) for leading references; (b) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 909 (1960); (c) R. Lukes and V. Dedek, *Coll. Czechoslov. Chem. Commun.*, **25**, 1174 (1960); (d) S. Hunig and W. Lendle, *Ber.*, **93**, 909 (1960); (e) O. Cervinka, *Coll. Czechoslov. Chem. Commun.*, **24**, 1880 (1959); (f) G. Opitz, H. Hellmann, and H. Schubert, *Ann.*, **623**, 117 (1959); (*g*) Z. Eckstein, A. Sacha, and W. Sobotka, *Bull. acad. polon. sci., Serie des chim. geol. and geogr.*, **7**, 295 (1959).

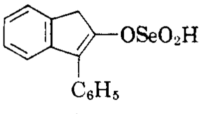
(4) All attempts at direct alkylation of I with chloromethyl benzyl ether in the presence of such bases as potassium tert-butoxide, and sodium hydride were unsuccessful (A. T. Blomquist and Y. C. Meinwald, unpublished information).

(5) A. C. B. Smith and W. Wilson, *J. Chem. Soc.*, 1342 (1955).

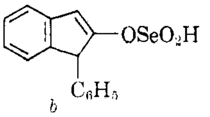
(6) The only systematic study of C- *vs.* *N*-alkylation has been made by G. Stork, ***Enamines as Synthetic Tools***, Abstracts of the Sixteenth National Organic Chemistry Symposium, June 1959, Seattle, Wash., p. 48. Stork alkylated pyrrolidine, piperidine, hexamethyleneimine, heptamethyleneimine, and morpholine enamines of cyclohexanone with methyl iodide, and obtained 2-methylcyclohexanone (based on unrecovered cyclohexanone) in 29%, 11%, 47%, 30%, and 27% yields, respectively.

(7) Although the alternative possibility, 3-hydroxy-1-phenyl-2-indanone, is not completely excluded, it is unlikely that the oxidation would stop at this α-hydroxy ketone step without proceeding to the 1,2-diketone, under the reaction conditions employed.

(8) A reflection of the greater conjugation (and consequent stability) of intermediate *a* over *b*



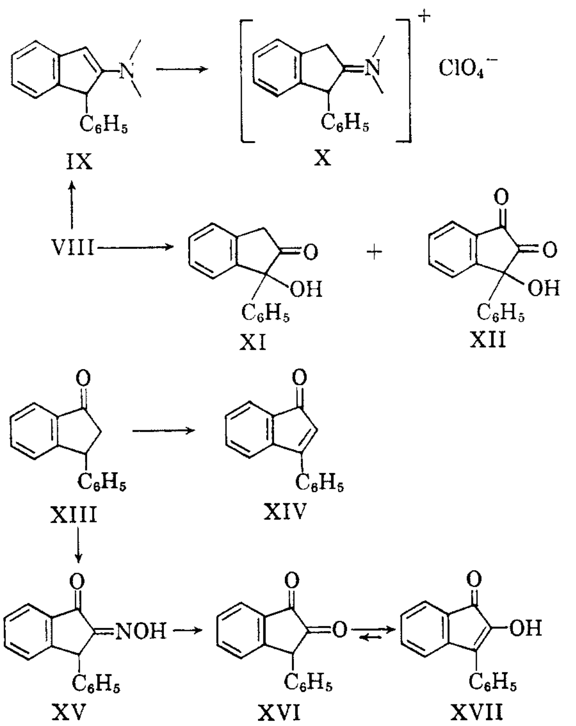
a



b

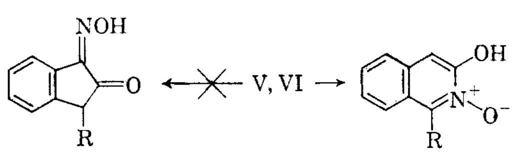
and product XIV over XVI [E. J. Corey and J. P. Schaeffer, *J. Am. Chem. Soc.* **82**, 918 (1960)].

(9) XVI was prepared in 79% yield by the pyruvic acid hydrolysis of 2-oximino-3-phenyl-1-indanone(XV).[10,11]



Recent work on the photolysis of 2-diazo-1-indanones has led to a series of ring-contracted benzocyclobutene-1-carboxylic acids.[12–14] All the diazoindanones irradiated[15] were prepared by treatment of an alkaline solution of the 2-diazo-1-indanones with chloramine (Forster reaction).[16] In an attempt to prepare the isomeric 1-diazo-2-indanone precursors (XX), V and VI were nitrosated under alkaline conditions to potassium salts which could be isolated. Acid hydrolysis of these salts gave yellow products, respectively, of molecular formula $C_{10}H_9O_2N$, and $C_{17}H_{15}O_3N$, each of which corresponded to the desired oximino ketone (XX: R = CH_3; R = $CH_2OCH_2C_6H_5$). Although these compounds displayed moderate OH bands (2.96–2.97 μ), and strong C=N bands (6.06–6.07 μ), no carbonyl bands were present[17] nor did the compounds react with chloramine to give the expected diazoketone. Further, both compounds gave a positive ferric chloride test and compound $C_{10}H_9O_2N$ formed a picrate in a 2:1 ratio.

Although compounds $C_{10}H_9O_2N$ and $C_{17}H_{15}O_3N$ were not further identified, alternative structures which fit the analytical, chemical and spectral data are the hydroxyisoquinoline *N*-oxides (XVIII, XIX).[18]



XVIII. R = CH_3
XIX. R = $CH_2OCH_2C_6H_5$

---

[10] XIII and the potassium salt of XV were graciously supplied by Charles G. Bottomley in quantity and with information on the idiosyncrasies of preparation and reactions.

[11] C. F. Koelsch, *J. Am. Chem. Soc.*, **58**, 1321 (1936).

[12] (a) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955); (b) L. Horner, W. Kirmse, and K. Muth, *Ber.*, **91**, 430 (1958).

[13] M. P. Cava, R. T. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

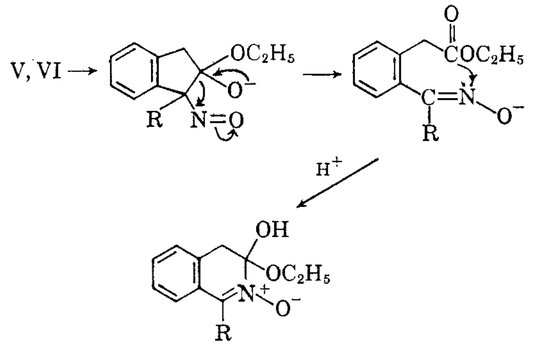
[14] A. T. Blomquist and C. Bottomley, unpublished information.

[15] Cava[13] has prepared 3,3-diphenyl-1-diazo-2-indanone by base decomposition of 3,3-diphenyl-2-oxo-1-tosylhydrazone, but apparently did not irradiate it.

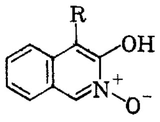
[16] M. O. Forster, *J. Chem. Soc.*, 971 (1925).

[17] As for example in 2-oximino-3-phenyl-1-indanone (XV) which showed a strong carbonyl band at 5.82 μ (potassium bromide).

[18] XVIII and XIX could be formed by nitrosation at the more sterically hindered α-carbon,[19] cleavage of the five-membered ring by potassium ethoxide,[20] followed by ring closure to form the hydroxyisoquinoline *N*-oxide.

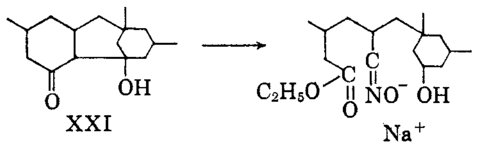


$\xrightarrow{-C_2H_5OH}$ XVIII, XIX. We are grateful to Professor George L. Buchanan, The University, Glasgow, for this suggestion. Nitrosation at the less sterically hindered α-carbon atom



would lead to the isomeric 4-alkyl-3-hydroxyisoquinoline *N*-oxides by the same mechanistic path. Results obtained in the selenium dioxide oxidation of VIII however strongly support the greater reactivity of the tertiary over the secondary α-carbon atoms.

[19] In an analogous case, nitrosation under basic conditions of a 3,4-dimethylcyclohex-2-enone dimer reduction product XXI



XXI

XXII

also occurred at the more substituted α-carbon atom followed by ring opening to form the sodium salt of the oximino ester (XXII) [W. A. Ayer and W. I. Taylor, *J. Chem. Soc.* 2227 (1955)].

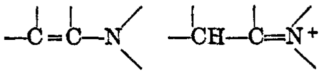
[20] J. C. Shivers and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 1264 (1947).

Thus this route to 1-diazo-2-indanones is not feasible but opens the possibility of a new pathway to isoquinoline derivatives. The scope of this reaction is under examination.

Spectral data. In the infrared, IIa–IId and IX showed strong maxima at 1567–1586 cm.$^{-1}$ (C=CN) (Table II). This is somewhat lower than previously observed for enamines,[21] and must be indicative of extended conjunction with the aromatic moiety of the indanone system. Further, the identity in frequency between IIc and IX strongly suggests that the phenyl substituent in IX as indicated is not conjugated with the ternary amine moiety.[23,27] The perchlorate salts (IIIa–IIId, and X) absorb characteristically in the range 1675–1717 cm.$^{-1}$ [8b,22] (C=N$^+$=). The large shifts (108–131 cm.$^{-1}$) of the double bond stretching maximum in going from the α,β-unsaturated amines to their respective ternary iminium salts,[24] can be attributed to the double bond shift exocyclic to the five-membered ring and out of conjugation with the aromatic moiety.

TABLE II

DOUBLE BOND STRETCHING MAXIMA (INFRARED) AND FREQUENCY SHIFTS OF ENAMINES AND THEIR PERCHLORATE SALTS IN CM.$^{-1}$

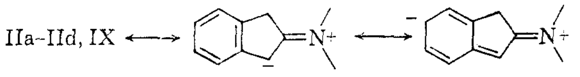


$$-\overset{|}{C}=\overset{|}{C}-N\langle \qquad -\overset{|}{C}H-\overset{|}{C}=N^{+}\langle$$

Indenes	Enamine[a]	Perchlorate[a]	Δν
2-(*N*-Pyrrolidyl)	IIa: 1586	IIIa: 1717	131
2-(*N*-Piperidyl)	IIb: 1569	IIIb: 1700	131
2-(*N*-Hexamethylene-imino)	IIc: 1567	IIIc: 1692	125
2-(*N*-Morpholinyl)	IId: 1573	IIId: 1704	131
3-Phenyl-2-(*N*-hexamethyleneimino)	IX: 1567	X: 1675	108

[a] Obtained on a Nujol mull. [b] In a potassium bromide wafer, the enamine and perchlorate absorbed respectively, at 1588 cm.$^{-1}$ and 1716 cm.$^{-1}$; $\Delta\nu$ = 128 cm.$^{-1}$

In the ultraviolet all the enamines displayed two maxima: a broad band at 224–227 mμ[25,26] consigned to excited structures such as XXIII, and an equally broad band of greater intensity at longer wavelength (291–303 mμ) (Table III). The essential coplanarity of the 2-indanone enamine system permits of an extension of the conjugated system to include such structures as XXIV. Hence, the new band at longer wave length.[27,28]



XXIII XXIV

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF ENAMINES IN CYCLOHEXANE

Enamines	λ(mμ)	ε	λ(mμ)	ε	λ(mμ)	ε
IIa			227	10,800	298	24,900
IIb			226	12,500	295	21,900
IIc			227	11,600	303	28,000
IId	214	6,700	224	6,200	291	9,000
IX	220	17,000	231	17,000	303	22,000

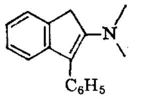
2-Indanone (I) and its derivatives V, VI, VII, VIII, and XI displayed a trio of characteristic bands at 262–263 mμ, 268–269 mμ, and 275–276 mμ (Table IV) which is surely benzenoid absorption. In the infrared, solid state, and (where possible) film spectra of I, V, VI, VII, VIII, and XIII showed no hydroxyl absorption and these compounds must exist completely in the keto form (Table V). In carbon tetrachloride solvent (carefully dried), I, V, VI, and VII displayed weak hydroxyl bands indicating some slight degree of enolization in solution. 3-Phenyl-1,2-indandione (XVI) (potassium bromide) showed a strong,

---

[21] N. J. Leonard and his students[22] reported absorption maxima of 1630–1666 cm.$^{-1}$ for substituted Δ^2-tetrahydropyridines (this double bond frequency shows a dependence upon substitution on the double bond), and Δ^2-tetrahydropyrrolines. Kuehne[8a] reported 1630–1640 cm.$^{-1}$ for enamines of cyclic ketones (C_4—C_9), while Speziale and Freeman[8b] report 1612 cm.$^{-1}$ for *N*,*N*-diethyl-1,2,2-trichlorovinylamine.

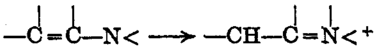
[22] (a) N. J. Leonard and F. P. Hauck, *J. Am. Chem. Soc.*, 79, 5279 (1957); (b) N. J. Leonard and V. W. Gash, *J. Am. Chem. Soc.*, 76, 2781 (1954).

[23] The completely conjugated



would undoubtedly absorb at lower frequency. *Cf.* 2-benzyl-1-methyl-Δ^2-tetrahydropyridine (1645 cm.$^{-1}$) with the 2-phenyl derivative (1630 cm.$^{-1}$).[22a]

[24] Corresponding to the reaction



$$-\overset{|}{C}=\overset{|}{C}-N< \longrightarrow -CH-\overset{|}{C}=\overset{|}{N}<^{+}$$

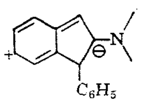
reported shifts range from 20–62 cm.$^{-1}$.[8b,22]

[25] See N. J. Leonard and D. M. Locke, *J. Am. Chem. Soc.*, 77, 437 (1955) for leading references.

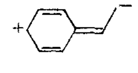
[26] E. Benzig, *Angew. Chem.*, 71, 521 (1959).

[27] The effect of conjugation on wave length and extinction is strikingly demonstrated on comparison of the ultraviolet maximum and extinction of *N*-cyclohexyl-*N*-methylenamine of isobutyraldehyde (230–231 mμ, ε 2600) with the *N*-phenyl-*N*-methylenamine (263–265 mμ, ε 13,750).[26] *Cf.* also the small difference (4 μ) actually observed between IIc and IX in the ultraviolet.

[28] The high extinction and wave length of the 220 mμ band in IX may be considered as derived from a benzene B-band chromophore [W. F. Forbes and R. Shilton, ASTM Special Technical Publication No. 269 Symposium on Spectroscopy, 176 (1960)]. The band at 214 mμ (ε 6,700 is in the styrene absorption range [211 mμ, ε 16,000; 224 mμ; ε 12,000] and suggests the electronically excited structure



i.e., as in styrene



It is quite possible that the bands in the 214–220 mμ range correspond to the band at 211 mμ in styrene (Dr. W. F. Forbes, private communication).

associated hydroxyl band at 3.03 μ and a single, sharp carbonyl band at 5.82 μ supporting the massive chemical evidence that this compound exists completely in the enolic form as 2-hydroxy-3-phenylindone (XVII).[11] In chloroform solution this association and enolization decreases, and the hydroxyl band appears as a weak band at 2.92 μ with the second carbonyl band appearing as a shoulder at 5.78 μ. When enolization is prevented as in 3-hydroxy-3-phenyl-1,2-indandione (XII), the expected strong carbonyl doublet appears at 5.67 μ and 5.77 μ. The most unique feature of the infrared absorption spectra of the 2-indanone ring system was the display of *two carbonyl bands* in carbon tetrachloride solutions of I, V, VI, VII, VIII, and XI.[31] These bands of varying intensity in the 5.64–5.69-μ, and 5.69–5.78-μ regions[29] are reminiscent of similar anomalous infrared spectra of some cyclopentenones,[30a] unsaturated lactones[30b] and cyclopentanones.[30c] As the bifurcation was observed in both solid state and film spectra, the possibility of rotational isomerization seems unlikely. The general instability of 2-indanones however does not preclude the possibility of carbonyl impurities. Finally, the possibility of Fermi resonance[30,33] between the carbonyl vibration and a close-lying overtone also must be considered since all these compounds except I[34] show weak bands in the 11.30–11.40-μ region. To date we have been unable to make any single assignment of these latter bands which could account for the observed doublet, *and* for the presence only of single carbonyl bands in 3-phenyl-1-indanone (XIII), 3-phenylindone (XIV) (which has a single ethylenic C—H bond), and *cis*-3,4-diphenyl-2-cyclopenten-1-one.[30a]

EXPERIMENTAL[35]

2-Indanone (I) was prepared from Fluka indene *via trans*-2-bromo-1-indanol[36] and *trans*-1-methoxy-2-indanol[37] in an average over-all yield of 56% (ten runs). The distilled intermediate, *trans*-1-methoxy-2-indanol,[37b] 96–98° (0.5 mm.), 121–122° (1.4 mm.), 118–119° (0.9 mm.), could be stored indefinitely. Acid hydrolysis of *trans*-1-methoxy-2-indanol[37b] followed by steam distillation[38] gave fragrant white needles of I, m.p. 54.5–55.0° [b.p. 54–56°(0.1–0.2 mm.)]. The compound thus prepared was used directly. One recrystallization from petroleum ether (b.p. 30–60°) however raised the m.p. to 55.0–55.5° (lit.,[36,37a] m.p. 56–57°; 58% yield from indene).

1,3-Dioximino-2-indanone was prepared using Cava's procedure[13] and crystallized from ethanol-water as tan needles, m.p. 265–267° dec (lit.[40] m.p. 233°).

Anal. Calcd. for $C_9H_6N_2O_3$: C, 56.84; H, 3.18. Found: C, 56.77; 56.87; H, 3.23, 3,30.

Bromomethyl benzyl ether. The directions for preparing chloromethyl benzyl ether[41] were generally followed: while cooling in an ice bath, 250 g. (2.31 moles) of Eastman No. 40 (chlorine free) benzyl alcohol and 535 ml. (564 g., 6.93 moles) of 36–38% formaldehyde solution were mixed to form a clear solution. Hydrogen bromide gas was passed into the solution to saturation during which time the reaction mixture separated into two layers. When the two phase mixture was poured into a separatory funnel, the yellow bromomethyl benzyl ether solution was now the heavier phase. The lower layer was separated, dried overnight over anhydrous calcium chloride, decanted and distilled *in vacuo*. The 69–82° (0.65–0.85 mm.) fraction was collected and redistilled to give colorless bromomethyl benzyl ether, b.p. 45–46° (0.15 mm) in 60% yield. This α-bromo ether gave an instantaneous silver bromide precipitate with aqueous silver nitrate.

Anal. Calcd. for C_8H_9OBr: C, 47.78; H, 4.51. Found: C, 48.05; H, 4.29.

This preparation must be performed in an efficient hood as the bromoether is a powerful lachrymator, inhalation of which even in small amounts causes severe headaches. On the skin it produces a burning sensation.

During the first distillation a formaldehyde polymer coated the entire distillation apparatus. It was most conveniently removed with *aqua regia* (*hood*).

General procedure for the preparation of enamines IIa–IId. In a three necked, 500-ml. flask fitted with a magnetic stirrer, water trap, reflux condenser, nitrogen inlet, and heating mantle, a solution of 0.20 mole of the secondary amine and 100 ml. of thiophene-free benzene was refluxed until all the water had been removed from both solvent and reactant. 2-Indanone (I) (13.2 g., 0.10 mole) was then added in one portion, and the variously colored solution (yellow, red, brown) was refluxed until the separation of water had ceased. More than the theoretical amount of water appeared

---

[29] In potassium bromide wafers this band appeared at 5.77–5.83 μ, while in a film at 5.70–5.78 μ.

[30] (a) P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958); P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958); (b) R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can. J. Chem.* **37**, 2007 (1959); (c) C. L. Angell, P. J. Kreuger, R. Lauzon, L. C. Leitch, K. Novack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta.*, **11**, 926 (1959).

[31] On the basis of carbonyl group frequency shifts of 1-bromo- and 1-chloro-2-indanone relative to I, Brutcher and co-workers[32] have suggested that the 1-halo-2-indanones are planar. They report however only one carbonyl frequency for each of these compounds.

[32] F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.* **81**, 4915 (1959).

[33] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, VanNostrand, New York, 1945, p. 215; E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955, p. 198.

[34] In carbon tetrachloride solution, the 11–15 μ area is blank.

[35] Melting points were taken on a Fisher-Johns apparatus calibrated with A. H. Thomas test reagents. Boiling points are uncorrected. Infrared and ultraviolet spectra were obtained, respectively, on a Perkin-Elmer Model 21 and a Beckman Model DK. All analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[36] C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.* **62**, 3473 (1940); *trans*-2-bromo-1-indanone was used without further purification. An analytically pure sample could be obtained on recrystallization from boiling water, in which it is only moderately soluble; at this temperature it is also a mild lachrymator.

[37] (a) N. Levin, B. E. Graham, and H. G. Kolloff, *J. Org. Chem.*, **9**, 380 (1944); (b) W. Treibs and W. Schroth, *Ann.* **639**, 204 (1961).

[38] The universal steam distillation apparatus described by F. T. Wallenberger and co-workers was used effectively.[39]

[39] F. T. Wallenberger, W. F. O'Connor, and E. J. Moriconi, *J. Chem. Ed.*, **36**, 251 (1959).

[40] F. Heusler and H. Schieffer, *Ber.*, **321**, 28 (1899).

[41] A. J. Hill and D. T. Keach, *J. Am. Chem. Soc.*, **48**, 257 (1926).

since the 2-indanone was stored at −28°, and water condensed on it while weighing.

2-(N-Pyrrolidyl)indene (IIa). Still protected from air, the greenish red, fluorescent solution was evaporated to dryness (Rinco), the residue was taken up in about 200–300 ml. of anhydrous ether, and chromatographed (Woelm's basic aluminum oxide, Activity Grade 1) with anhydrous ether as the eluant. A minimum of four elutions, each with about 500 ml. of anhydrous ether through freshly prepared 15″ × 7/8″ columns was required to obtain an off-white product, m.p. 117–119°, in 92% (19.3 g.) yield. Analytically pure IIa, m.p. 120–121°, was obtained by evaporating a center cut. It is advisable to complete *all* enamine preparations without interruption, as in solution they seem quite sensitive to air oxidation to yield a beautiful, blue-violet colored solution. This blue-violet impurity (present in less than 1% concentration) persisted throughout the chromatographic purification, and was almost as easily eluted as the enamine.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.48; H, 8.33.

The perchlorate salt of IIa (IIIa). A solution composed of 25 ml. 70% perchloric acid solution (Baker and Adamson No. 1144) and 25 ml. of absolute ethanol was added to an ethereal solution of IIa to the blue color of Congo Red paper (*p*H <3).[42] The perchlorate salt IIIa precipitated immediately. One recrystallization from acetone gave colorless plates, m.p. 207–211° dec.[43]

Anal. Calcd. for $C_{13}H_{16}NClO_4$: C, 54.67; H, 5.61; N, 4.91. Found: C, 54.51; H, 5.82; N, 5.16.

2-(N-Piperidyl)indene (IIb) was obtained in 90% yield after only two chromatographic treatments as colorless plates, m.p. 98–99°, lit. m.p., 102°.[37b]

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.30; H, 8.56.

The perchlorate of IIb (IIIb) crystallized from acetone as colorless plates, m.p. 187–192° dec.

Anal. Calcd. for $C_{14}H_{18}NO_4Cl$: C, 56.09; H, 6.05; N, 4.67. Found: C, 55.92; H, 6.06; N, 4.65.

2-(N-Hexamethyleneimino)indene (IIc). The yellow enamine solution was evaporated to dryness (Rinco) to leave impure IIc as a liquid sludge. This was dissolved in a minimum amount of benzene and twice chromatographed (Woelm's basic aluminum oxide, Activity Grade 1) with benzene as the eluant. Recrystallizations from anhydrous ether, and then petroleum ether gave IIc in 85% yield as colorless plates, m.p. 106.5–107°, lit. m.p., 106°.[37b]

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.49; H, 8.98; N, 6.57. mol. wt., 213. Found: C, 84.45; H, 8.80; N, 6.78; mol. wt., 195 (Rast).

The perchlorate of IIc (IIIc) crystallized from acetone-anhydrous ether as colorless plates, m.p. 192–197° dec.

Anal. Calcd. for $C_{15}H_{20}NClO_4$: C, 57.41; H, 6.42; N, 4.46. Found: C, 57.60; H, 6.66; N, 4.76.

2-(N-Morpholinyl)indene (IId). The yellow enamine solution was cooled whereupon crude IId separated in 90% yield. Two recrystallizations from benzene gave white crystals, m.p. 197–198°.

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.28; H, 7.81.

The perchlorate of IId (IIId) crystallized from acetone-anhydrous ether as colorless rods, m.p. 208–213° dec.

Anal. Calcd. for $C_{13}H_{16}NO_5Cl$: C, 51.74; H, 5.35; N, 4.64. Found: C, 51.87; H, 5.39; N, 4.94.

General procedure for the alkylation of enamines IIa–IId. In the preparation of V, VI, and VII, enamine IIc was alkylated with the appropriate alkyl halide. In the C- vs. N-alkylation studies, enamines IIa–IId were alkylated with bromomethyl benzyl ether (Table I). The enamine in solution was prepared as previously described. Still protected from air and moisture, the greenish red fluorescent solution was evaporated to dryness (Rinco) and the crude yellow enamine under nitrogen was dissolved in 100 ml. of dry dioxanetetrahydrofuran (50:50). Crude IIa–IIc dissolved at room temperature while IId was soluble only at reflux temperature. To a solution of IIa–IIc at room temperature was added dropwise (15–30 min.) 0.15 mole of the alkyl halide (methyl iodide, bromomethyl benzyl ether, and benzyl bromide) followed by a 10–15 ml. tetrahydrofuran wash of the separatory funnel. The reaction was initially exothermic after which the solution was slowly heated to reflux (80–87°). The white to tan, insoluble iminium salt[44] appeared during the addition of the alkyl halide or on warming, and continued to deposit as the suspension was heated at reflux for 3–5 hr. Bromomethyl benzyl ether was added directly to a refluxing solution of crude IId in dioxane-tetrahydrofuran.

The suspension was cooled to room temperature, whereupon 100 ml. of water was added. The iminium salt dissolved to give an oily suspension which was further stirred at room temperture for 14–20 hr. to yield two easily separable layers. Both layers were extracted with a total of 200–300 ml. of ether. The ether extracts were dried overnight with anhydrous sodium sulfate, filtered, evaporated (Rinco), and the dark liquid residue vacuum distilled. The first fractions contained solvents, unchanged alkyl halide and its hydrolysis product, and 2-indanone (see Table I) fol-

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA OF 2-INDANONES
(Values *in italics* represent inflections in this table)

Compound	λ_{max} (mμ)[a]	ϵ_{max}
Indanone (I)[b]	*256*	*400*
	262	800
	269	1400
	275	1600
1-Methyl-2-indanone (V)[c]	246	400
	255	*500*
	262	800
	268	1200
	275	1400
1-Benzyloxymethyl-2-indanone (VI)	*256*	*600*
	262	900
	269	1300
	275	1500
1-Benzyl-2-indanone (VII)	263	1800
	269	1900
	276	1700
	ca. *310*	*500*
1-Phenyl-2-indanone (VIII)[d]	*256*	*700*
	262	1000
	269	1300
	275	1400
1-Hydroxy-1-phenyl-2-indanone (XI)[e]	262	1100
	269	1500
	276	1500
	310[f]	500

[a] In cyclohexane unless otherwise noted. [c] D. Biquard, *Bull. soc. chim. France* [*5*] 8, 55 (1941) reported only $\lambda_{max}^{C_6H_{12}}$ 268 mμ (log ϵ, *ca.* 3.01); 268 mμ (log ϵ, *ca.* 3.02). [c] Other bands include: 292 mμ (ϵ 200), 300 mμ (ϵ 200). [d] Other bands are at: 293 mμ, 303 mμ, and 314 mμ. All have ϵ's of 200. [e] In 95% ethanol. [f] Broad band.

---

(42) This procedure was suggested by Dr. A. G. Cook, Valparaiso University, Dept. of Chemistry.

(43) The perchlorate salts of all the enamines brown or discolor before melting with decomposition.

(44)

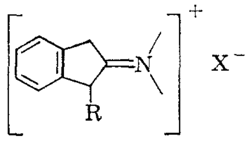


TABLE V

HYDROXYL AND CARBONYL ABSORPTION MAXIMA OF 1- AND 2-INDANONES, AND 1,2-INDANDIONES

	OH (μ)			C=O (μ)		
Compound	Film	Solution^a	KBr	Film	Solution^a	KBr
2-Indanone (I)	—^{b}	2.91 (vw)	—^{b}		5.69 (s), 5.78 (w)	5.71 (s), 5.78 (w)
1-Methyl-2-indanone (V)	—^{b}	2.92 (w)		5.68 (s), 5.70 (s)	5.64 (s), 5.69 (s)	
1-Benzyloxymethyl-2-indanone (VI)	—^{b}	2.90 (vw)		5.68 (s), 5.73 (s)	5.67 (s), 5.72 (s)	
1-Benzyl-2-indanone (VII)	—^{b}	2.89 (vw)		5.68 (s), 5.70 (s)	5.67 (s), 5.69 (s)	
1-Phenyl-2-indanone (VIII)	—^{b}	—^{b}	—^{b}	5.67(s), 5.78 (m)	5.66 (s), 5.78 (m)^e	5.69 (s), 5.78 (m)
1-Hydroxy-1-phenyl-2-indanone (XI)			2.93 (s)			5.72 (s), 5.83 (m)
3-Hydroxy-3-phenyl-1,2-indandione (XII)			2.96 (s)			5.66 (s), 5.77 (s)
1,3-Dioximino-2-indanone			3.15–3.35 (s)^c			5.68 (s)
3-Phenyl-1-indanone (XIII)			—^{b}			5.83 (s)
2-Oximino-3-phenyl-1-indanone(XV)			3.04 (s)^d			5.82 (s)
3-Phenylindone (XIV)		—^{b}	—^{b}		5.79 (s)	5.83 (s)
3-Phenyl-1,2-indandione (XVI)		2.92 (w)^g	3.03(s)^d		5.78 (s),^{f,g} 5.82 (s)^g	5.84 (s)

[a] In carbon tetrachloride solvent previously dried over phosphorus pentoxide. [b] No OH absorption observed. [c] Broad band; probably combination of C—H and associated OH. [d] Associated OH. [e] Solution of liquid VIII. [f] Shoulder. [g] Chloroform solution.

lowed by the desired C-alkylated 2-indanone. In most cases, a red-orange, higher-boiling fraction was obtained which on the basis of infrared spectra seemed to be 2-indanone self-condensation products.

In general, all the 2-indanones were easily oxidized by air to dark colored products. I and VIII in the solid state could be kept carefully stored under nitrogen at room temperature several months before decomposition began. V-VIII in the liquid state, even with the most rigid exclusion of air, began to darken and discolor at room temperature within an hour after preparation. Storage at −28° immediately after preparation minimized this visible sign of decomposition but did not prevent it. All attempts to crystallize V, VI, and VII from anhydrous solvents, ethanol, ether, and petroleum ether (b.p. 30–60°) were unsuccessful. Absorption spectra of I and V-VIII (Tables IV and V) were taken immediately after preparation.

1-Methyl-2-indanone (V) was obtained in 40% yield as a light yellow oil, 140–143° (3.5–3.7 mm.), 154–155° (7.8 mm.). Even under nitrogen at −28°, V turned black overnight.

The semicarbazone of V was obtained as creamy white crystals after two recrystallizations from ethanol-water; m.p. 197.5–199.5° dec.

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.44; N, 20.68. Found: C, 65.16; H, 6.35; N, 20.94.

1-Benzyloxymethyl-2-indanone (VI) distilled as an orange-yellow oil, 162–166° (1.8–2.0 mm.) in 39% yield.

The semicarbazone of VI was obtained as an aggregate of white crystals after two recrystallizations (slow) from absolute methanol; m.p. 181–183° dec.

Anal. Calcd. for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58; mol. wt., 309. Found: C, 69.66; H, 5.93; N, 13.77; mol. wt., 302 (Rast).

1-Benzyl-2-indanone (VII) was obtained in the 210–233° (1.4–1.6 mm.) fraction. The high distillation temperature resulted in continuous decomposition during which the temperature fluctuated erratically. The dark oil (33% yield) under nitrogen was dissolved in anhydrous ether (some insoluble material remained) and briefly warmed with aluminum oxide (Woelm's neutral, Activity Grade I) and charcoal, filtered, dried over anhydrous sodium sulfate, and evaporated to give a clear brown oil in 20% yield.

The 2,4-dinitrophenylhydrazone of VII was prepared using Shine's procedure[45] and crystallized as red needles from bis-2-methoxyethyl ether-absolute ethanol; m.p. 230–231° dec.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.66; H, 4.29; N, 13.78.

1-Phenyl-2-indanone (VIII), b.p.'s 147–150° (0.7 mm.), 164–167° (2.4–2.5 mm.); m.p. 49–50° (lit.[5] b.p. 130–135° (0.2 mm.); m.p. 51–53°) was obtained from Eastman (P-974) 1,3-diphenyl-2-propanone (IV) in two steps without purification of the intermediate 1-bromo-1,3-diphenyl-2-propanone. Thus, to a stirred mixture of 100 g. (0.476 mole) of IV, 350 ml of carbon disulfide, and 48 g. (0.48 mole) of calcium carbonate at room temperature was added 24.4 ml. (0.48 mole) of bromine over a 30 min. period. After a brief induction period, the reaction proceeded smoothly with some hydrogen bromide gas evolving from the reflux condenser. Stirring was continued for an additional 2 hr. at which time the gas evolution had ceased. Water (150 ml.) was added to give a yellow suspension which was suction filtered. The orange carbon disulfide layer was then dried over anhydrous sodium sulfate, and filtered. This orange solution of 1-bromo-1,3-diphenyl-2-propanone was added over a 90-min. period to a cold (ice bath), stirred suspension of 116.7 g. (0.876 mole) of anhydrous, sublimed aluminum chloride in 250 ml. of carbon disulfide. The mixture was stirred for an additional 1 hr. at ice bath temperature and for 4 hr. at room temperature. A dilute hydrochloric acid solution (160 ml. of water and 40 ml. of concd. hydrochloric acid) was *slowly* added with vigorous stirring followed by an additional 200 ml. of water to dissolve as much as possible the gummy residue and to facilitate filtration. The two phase mixture was filtered, and the carbon disulfide layer dried over anhydrous sodium

---

(45) H. J. Shine, *J. Org. Chem.*, 24, 252 (1959).

sulfate. Filtration, evaporation, and vacuum distillation gave VIII as a yellow oil in 71% yield.

The semicarbazone of VIII was obtained as colorless rods after recrystallization from absolute ethanol; m.p. 207–210° dec. (lit. m.p. 200–202°[6]; 207–208° [46]).

Anal. Calcd. for $C_{16}H_{15}ON_3$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.77; H, 5.87; N, 16.10.

1-Phenyl-2-(N-hexamethyleneimino)indene (IX). Using the general preparative method of enamines IIa–IId, 10.4 g. (0.05 mole) of VIII gave 8.5 g. (59%) of crude enamine IX in the following manner. After the reaction was complete, and the solution evaporated to dryness, the impure enamine was dissolved in anhydrous ether and chromatographed over aluminum oxide (Woelm's basic, Activity Grade 1) with anhydrous ether as eluant. The blue-violet impurity, however, was co-eluted. The ethereal solution was then evaporated to dryness, the residue dissolved in petroleum ether (b.p. 30–60°) and the whole permitted to crystallize overnight at −28°. The blue-violet mother liquors were decanted and crude IX was twice recrystallized in the same manner from petroleum ether (b.p. 30–60°) (charcoal) to give IX as white rods; m.p. 72–73°.

Anal. Calcd. for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84; mol. wt. 289. Found: C, 87.37; H, 8.25; N, 5.10; mol. wt., 288 (Rast)

The perchlorate of IX (X) crystallized from acetone as colorless prisms; m.p. 200.5–202.5° dec.

Anal. Calcd. for $C_{21}H_{24}NClO_4$: C, 64.69; H, 6.20; N, 3.59. Found: C, 64.93; H, 6.35; N, 3.80.

Selenium dioxide oxidation of VIII. Freshly sublimed selenium dioxide (14.4 g., 0.130 mole) was dissolved with stirring in 200 ml. of 95% ethanol and 3.1 ml. of water, and warming to *ca.* 40°. VIII (25.0 g., 0.12 mole) was added in one portion and the solution was stirred for 5 hr. at 55–60°. The precipitated selenium residue was filtered, and the ethanolic filtrate evaporated to 25–35 ml. This was added with stirring to 1 l. of ice water and the suspension refrigerated overnight. Filtration gave both solid and a red gum. The selenium residue, solid, and gum were first extracted with 400 ml. of boiling petroleum ether (b.p. 90–100°) (three portions), and then extracted with 500 ml. (four portions) of ether.

The orange petroleum ether extracts were evaporated to one-half their volume, treated with charcoal, filtered and refrigerated to yield 1.5 g. (6%) of crude *1-hydroxy-1-phenyl-2-indanone* (XI), m.p. 118–121°. Two further recrystallizations from the same solvent (charcoal) gave analytically pure XI as orange chunks; m.p. 131–132°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39; mol. wt. 224. Found: C, 80.56; H, 5.51; mol. wt., 225 (Rast).

The semicarbazone of XI was obtained as pink prisms, from ethanol-water; m.p. 200–201.5° dec.

Anal. Calcd. for $C_{16}H_{15}O_2N_3$: C, 68.31; H, 5.27; N, 14.94. Found: C, 68.10; H, 5.48; N, 14.75.

The ether extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness to yield 3.09 g. (11%) of crude, red-violet XII; m.p. 138–153°. Two recrystallizations from acetic acid–water gave red XII m.p. 241–250° dec. In the recrystallization, crude XII was added to cold acetic acid, the whole brought to a boil, and boiling water added to saturation. The suspension was filtered while hot, and the solution cooled slowly. In this manner, the extensive decomposition which occurred on heating in acetic acid was kept at a minimum. The fraction, m.p. 241–250°, gave the best analysis reported below. Each recrystallization raised the m.p. 10–15° and ultimately a red product, m.p. 260–267° dec., could be obtained with an infrared spectrum quite similar to the lower melting product. Analyses, however, were erratic. A shorter reaction time (4 hr.) gave a 9% yield of XI and a 3% yield of XII.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.15; H, 4.39.

Selenium dioxide oxidation of 3-phenyl-1-indanone[10] (XIII). A solution of 5.0 g. (0.024 mole) of XIII, 40 ml. of 95% ethanol, 0.75 ml. of water, and 2.88 g. of freshly sublimed selenium dioxide (0.025 mole) was stirred for 6 hr. at 60°. The precipitated selenium was filtered, and the red solution was added with stirring to 500 ml. of water. The orange suspension and red gum were refrigerated overnight and filtered; the red gum adhering to both flask and filter paper, and the selenium residue were extracted with 200 ml. of anhydrous ether. The extracts were dried over anhydrous sodium sulfate, concentrated and chromatographed (nonalkaline aluminum oxide, Woelm's Activity Grade 1) with ether as eluant. The first red zone was eluted, and evaporated to dryness to give a red oil. The next zone (blue) was left on the column. The red oil was dissolved in boiling absolute ethanol and cooled slowly to yield 0.3 g. of crude *3-phenylindone* (XIV) as red-orange flakes; the addition of increasing amounts of water gave four additional fractions of crude XIV, m.p. range 60–80°. The first two fractions were combined and twice recrystallized from absolute ethanol (some indone always gummed on heating) to give a red-orange powder, m.p. 104–111°. Neither the red oil, nor any crystallized fraction ever gave a correct analysis for XIV. Rast mol. wts. for all fractions averaged 219 (calcd. for $C_{15}H_{10}O$, mol. wt. 206).[47] From each fraction, however, the *semicarbazone of* XIV could be obtained as colorless prisms after 2-3 recrystallizations (charcoal) from absolute ethanol; m.p. 212–214° dec.

Anal. Calcd. for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.97; N, 15.96. Found: C, 73.18; H, 5.14; N, 15.88.

2-Oximino-3-phenyl-1-indanone (XV) was prepared by the acetic acid hydrolysis of the potassium salt of XV[10] and obtained as creamy white, fluffy needles; m.p. 211–216.5° dec. from acetone-water (lit.[11] m.p. 198–203°).

3-Phenyl-1,2-indandione (XVI) was obtained in 79% yield as black violet needles, m.p. 138–144°, using Koelsch's procedure[11] involving hydrolysis of XV in the presence of pyruric acid, water, acetic and hydrochloric acids; lit.[11] m.p. 140–147°. One attempt was made without success, using DePuy and Ponder's hydrolysis procedure for conjugated derivatives.[48] A 4.0-g. sample of XV was heated for 3 hr. at 70° with the required amount of levulinic acid-hydrochloric acid. As indicated[48] the oxime went into solution slowly to yield a deep red solution from which there was obtained a 78% recovery of XV. No XVI was isolated. It is most probable that much longer heating periods at perhaps higher temperatures are required for these conjugated keto-semicarbazones.

Treatment of V with n-butyl nitrite in potassium ethoxide. A solution of V (9.45 g., 0.0647 mole) in 15 ml. of absolute ethanol was added in one portion to an ice bath cooled, stirred solution of 2.54 g. (0.0650 g.-atom of potassium in 100 ml. of absolute ethanol under nitrogen. To this yellow solution was added 7.5 ml. (0.07 mole)of *n*-butyl nitrite over a 10-min. period; the first few drops of *n*-butyl nitrite produced a blood red solution and after about 1 hr. a yellow residue appeared. Stirring was continued for a total of 3 hr., after which the light yellow residue was filtered from mother liquor. The blood red filtrate was evaporated to dryness; the dark residue was dissolved in 500 ml. of ice water, and acidified to *p*H 1. The red-black residue was filtered (8.5 g.) and on drying *in vacuo* gave a black, amorphous gum which was not further investigated.

The light yellow residue was also dissolved in 500 ml. of

---

[46] A. S. Kende, *Chem. & Ind.* 1053 (1956).

[47] R. de Fasi, *Gazz. chem. ital.*, 49, II, 253 (1919) reported the isolation of XIV as a red-orange powder, m.p. 69–71°, by treatment of ethyl 3-hydroxy-3,3-diphenylpropanoate with sulfuric acid. Although he offered no analysis for his product, he was able to reduce this material with palladium on charcoal in acetic acid to give authentic 3-phenyl-1-indanone (XIII).

[48] C. H. De Puy and B. W. Ponder, *J. Am. Chem. Soc.*, 81, 4629 (1959).

ice water and acidified with dilute hydrochloric acid to give 1.17 g. (10%) of XVIII after filtration, as a yellow powder, m.p. 171–173°. One recrystallization from 95% ethanol gave dense yellow needles; m.p. 172–176° dec.

Anal. Calcd. for $C_{10}H_9O_2N$: C, 68.56: H, 5.18; N, 8.00; mol. wt., 175. Found: C, 68.78; H, 5.43; N, 8.30; mol. wt., 173.

An alcoholic solution of XVIII gave a deep red color with ferric chloride suggesting the presence of a phenolic hydroxyl group.[49] Although most oximes also give a red color with ferric chloride solution,[50] 2-indanone, XV, and 1,3-dioximino-2-indanone failed to give any color test with this reagent. The infrared spectrum potassium bromide showed a moderate OH band at 2.97 μ, and a strong band at 6.07 μ (C=N). Ultraviolet: $^{95\%}_{\max}$ 234 mμ (ϵ 3000), *ca.* 262 mμ[51] (ϵ 8000), 287 mμ (ϵ 4000), 303 mμ (ϵ 2700).

The picrate of XVIII was obtained as fluffy yellow needles after one recrystallization from 95% ethanol; m.p. 178–179° dec.

Anal. Calcd. for 2 $C_{10}H_9O_2N{:}C_6H_3O_7N_3$: C, 53.89; H, 3.65; N, 12.09. Found: C, 53.71; H, 3.72; N, 11.74.

Treatment of VI with n-butyl nitrite in potassium ethoxide. A solution of potassium ethoxide was prepared by dissolving 2.79 g. (0.014 g.-atom) of potassium in 95 ml. of absolute ethanol, under nitrogen, with stirring and external cooling (ice bath). VI (18.0 g., 0.714 mole) dissolved in 25 ml. of absolute ethanol was added in one portion. To the brown solution was added dropwise 9.35 ml. (8.26 g., 0.080 mole) of *n*-butyl nitrite over a 15-min. period. At first addition, the solution turned blood red, but after stirring for 3 hr. at 0°, the solution had turned green. The ethanolic solution was evaporated to dryness to yield a dark green residue which was dissolved in a minimum amount of carbon tetrachloride, and then reprecipitated with excess petroleum ether (b.p. 30–60°). The residue was suction-filtered, washed with petroleum ether (avoiding exposure to air a much as possible by keeping the residue covered with ether), and dried *in vacuo* to give a green potassium salt in 19.8 g. yield (87% based on $C_{17}H_{14}NO_3K$). Its infrared spectrum (potassium bromide) showed strong, broad bands at 2.99–3.15 μ (OH,CH) and 6.10–6.17 μ (C=N).

The potassium salt (1.0 g., 0.0031 mole) was dissolved in 20 ml. of ethanol and the whole externally cooled to 0°. Dilute hydrochloric acid was added dropwise with stirring to *p*H 1 during which time a grayish yellow residue appeared. Water (200 ml.) was added and the insoluble crude material (0.7 g., 80%) was filtered and washed with water. Successive crystallizations from 95% ethanol, and methanol gave XIX as soft yellow needles, m.p. range 109–126°.

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.77; H, 5.47; N, 5.14.

XIX gave a positive ferric chloride test and its infrared spectrum showed bands at 2.96 μ (m) (OH), and 6.06 μ (s) (C=N). Ultraviolet:
$\lambda_{\max}^{95\%\ C_2H_5OH}$ 227 mμ[52] (ϵ 41,900), *ca.* 262 mμ[51] (ϵ 12,400), 289 mμ (ϵ 4900), 303 mμ (ϵ 3300).

Acknowledgment. E. J. M. wishes to acknowledge with thanks the many provocative discourses with, and the stimulating company of his laboratory colleagues, Dr. G. L. Buchanan, Dr. A. G. Cook, and Dr. W. A. Hills.

ITHACA, N. Y.

---

(49) The unexpected yellow color and positive phenolic hydroxyl test of 3-hydroxyisoquinoline should be noted [J. H. Boyer and L. T. Wolford, *J. Org. Chem.*, 21, 1297 (1956)].

(50) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1956, p. 113.

(51) Inflection.

(52) Very broad band.

[CONTRIBUTION FROM THE PROTECTIVE DEVELOPMENT DIVISION OF THE U. S. ARMY CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES]

A New Synthetic Route to α-Isonitrosoacetonitriles. The Chlorination of Isonicotinaldehyde Oxime

EDWARD J. POZIOMEK AND ARTHUR R. MELVIN

Received February 6, 1961

A new synthetic route to aromatic and heteroaromatic α-isonitrosoacetonitriles has been found which involves chlorination of the appropriate aldoxime followed by reaction with excess alkali cyanide. The synthesis of a number of α-isonitrosoacetonitriles is presented; in addition, the chlorination of one of the aldoximes is described in detail. It was found that chlorination of isonicotinaldehyde oxime gave isonicotinohydroxamic chloride hydrochloride, which on neutralization with base yielded isonicotinohydroxamic chloride and 3,4-di(4-pyridyl)furoxan. The nitrile *N*-oxide of isonicotinonitrile is a logical intermediate in the synthesis of α-isonitroso-4-pyridineacetonitrile and 3,4-di(4-pyridyl)furoxan; however, no evidence of its formation was found.

During a Beckmann rearrangement study it was necessary to prepare a number of aromatic and heteroaromatic α-isonitrosoacetonitriles. Compounds of this oxime class have been prepared heretofore from the appropriate acetonitrile and alkyl nitrite[1] or nitric oxide,[2] from ω,ω′-dibromoaceto compounds by action of hydroxylamine and alkali,[3] or by boiling the appropriate glyoxime with sodium carbonate.[3] In addition a method limited to aliphatic compounds has been described which involves an oxidation of the reaction product of aldoximes and alkali cyanides.[4] We found the isonitrosation of acetonitriles described by Meyer[1]

---

[1] V. Meyer, *Ann.*, 250, 163 (1889).

[2] E. L. Reilly, U. S. Pat. 2,749,358 (1956); *Chem. Abstr.*, 51, 1269 (1957).

[3] (a) A. Russanov, *Ber.*, 24, 3504 (1891). (b) M. R. Zimmerman, *J. Pr. Chem.*, 66, 353 (1902).

[4] L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, 25, 1471 (1960).